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The authors have worked together since 1944 when Glass Science Inc. was founded. The period from 1944 to 1948 was devoted almost exclusively to research directly or indirectly related to glass problems. From 1948 until 1959, under a contract with the Office of Naval Research, they pursued basic research in the fields of fluorescence, semiconductors, surface chemistry, catalysis, and defect structures.

In July, 1959, they actively re-entered the field of glass technology research under a contract with the Glass Container Research Industry Corporation. The following paper, to be published in four parts, is an effort to define the conditions of glass formation and has led to conclusions which may be of considerable technological importance.

Conditions of Glass Formation Among Simple Compounds* IN FOUR PARTS

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Part I, Critical Review of Conventional Approaches to Glass Formation

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* Mineral Industries Contribution No. 59-95.

I. INTRODUCTION

● FOR SEVERAL HUNDRED YEARS the term *glass* was applied to the product which was obtained by melting a mixture consisting essentially of sand, alkali and limestone. In 1675 the flint glass was invented in England and, with this new type of glass, lead oxide became a major constituent of a group of glasses which was used for art ware and for optical instruments.

Later changes in the composition of glass were made primarily in order to produce glasses with new optical properties. With the work of Abbe and Schott (1880) a new period of glass melting began; ever since this time additional elements, such as lanthanum, were introduced into glasses primarily for obtaining a wider range of optical properties. Today commercial optical glasses are no longer limited to silica as the glass-forming oxide; borates and phosphates have become essential constituents of new types of glass. Glasses based on germanium dioxide were explored by L. M. Dennis and A. W. Laubengayer,[1] but their optical properties were not sufficiently different from silicate glasses to make it

worthwhile to develop them on a commercial basis.

The last decade has witnessed another great expansion of the field of glass compositions because of new interests in infrared-transmitting materials and in protective glasses which absorb gamma radiation or neutrons. Furthermore, recent developments in electronics called for low-melting glasses of high insulating power which can be used as a matrix for embedding electronic devices. For these purposes high transmission for visible radiation is no longer essential. This made possible the development of dark, but infrared-transmitting, glasses such as those based on the aluminates and ferrites of alkaline earths or those based on the deeply colored sulfides of arsenic and antimony. With respect to infrared transmission, the germanate glasses now become interesting.

The search for new types of glasses which absorb high energy radiation focused interest upon the development of glasses which contained a maximum amount of elements with high atomic numbers. Hitherto only PbO had been used for the manufacture of protective X-ray absorbing glasses, but now the composition range was extended to oxides such as TeO_2, Bi_2O_3, WO_3, or MoO_3. These substitutions widened our knowledge concerning the possibility of glass formation, but they also widened the gap which existed between our theoretical concepts concerning the conditions of glass formation on the one side and the experimental results on the other.

In the past, PbO stood fairly alone, it was the exception *par excellence* which defied one of the fundamental rules of glass formation; namely, that an orthosilicate cannot form a glass because its SiO_4 tetrahedra do not need to share corners. The participation of Pb^{2+} ions in the formation of a stable random three dimensional network was considered unlikely because the Pb^{2+} ion is too large for three- or four-fold coordination. Three- or four-fold coordination, however, was considered to be a prerequisite for the formation of stable glasses. PbO is no longer the only exception. G. W. Brady[2] (1957) found that a TeO_2 glass contained the tellurium atom in six-fold coordination. This glass which contained 98.15 wt per cent TeO_2 was found to be built according to the same principles as crystalline TeO_2. Brady remarked that the atomic structure of the tellurium glass violates the principles of glass formation as laid down in Zachariasen's rules.

Recently S. M. Brekhovskich[3] (1959) investigated the maximum amount of heavy metal ions which can participate in the formation of borate, phosphate and silicate glasses. For Bi_2O_3, for example, he found glass formation up to the ratios $2Bi_2O_3{\cdot}B_2O_3$ and $Bi_2O_3{\cdot}SiO_2$. Using a micro furnace he found that the Bi_2O_3 content of these glasses could be increased above these ratios if only milligram quantities were examined. Similarly, glasses were obtained for silicates, borates, and phosphates containing high concentrations of the "network-modifying" oxides CdO, PbO, ZnO and BaO. Brekhovskich arrived at the conclusion that Pb^{2+}, Bi^{3+}, Cd^{2+}, Zn^{2+}, and perhaps even Ba^{++} ions must be able to participate in the formation of the network.

In the past it has been convenient to subdivide the constituents of glasses into network-forming and network-modifying oxides. The first group, e.g., SiO_2, B_2O_3 and P_2O_5, were able to form glasses by themselves, whereas the second group, which could not be obtained in the glassy state, served to modify the properties of glasses. Network modifiers had to be combined with a major amount of a network former in order to produce a glass.

In contrast to the oxide of arsenic, that of antimony should not be called a glass former because molten Sb_2O_3 in gram quantities crystallizes on cooling. Nevertheless, W. A. Hedden and B. W. King[4] prepared glasses which contained close to 80 wt per cent Sb_2O_3, the rest being alumina and alkali. There can be no question that Sb_2O_3 must be the network-forming oxide in such a glass.

In contrast to arsenic trisulfide, pure antimony trisulfide does not form a glass. Nevertheless, B. W. King and G. D. Kelly[5] developed dark, infrared-transmitting glasses which contained approximately 95 per cent of a mixture of Sb_2O_3 and Sb_2S_3, the rest being K_2O.

Titanium dioxide does not form a glass by itself, but D. E. Harrison and F. A. Hummel[6] found that a mixture of TiO_2 and P_2O_5 in the ratio 3.5:1 forms a glass readily.

Pure vanadium pentoxide does not form a glass, but M. S. R. Heynes and H. Rawson[7] obtained a glass of the molar composition $PbO, 9V_2O_5$. In a similar way relatively small additions of P_2O_5 can transform V_2O_5 into a glass-forming oxide.

H. Rawson[8] found a similar situation in systems consisting of alkali and molybdic or tungstic oxide. In these systems narrow composition regions exist which have a tendency toward glass formation, whereas the pure oxides WO_3 and MoO_3 cannot be obtained as glasses, not even in very small quantities.

Many pure substances, e.g., PbF_2 or Pb_2GeO_4, when melted in a platinum crucible, crystallize on cooling. The same substances, melted for a short time in a porcelain crucible, form a glass because the small amounts of Al_2O_3 and SiO_2 which contaminate these melts prevent nucleation and crystallization. Lead orthogermanate, Pb_2GeO_4, had been reported to form a glass until L. Merker and H. Wondratschek[9] (1957) found that small amounts of impurities, especially Al_2O_3, are essential for glass formation.

J. E. Stanworth[10] (1954) in his attempts to produce a pure TeO_2 glass discovered that this oxide formed a glass when melted in an alumina crucible but not when melted in one of gold. The contamination of the TeO_2 by 8 per cent Al_2O_3 was responsible for glass formation.

The formation of stable* silicate glasses hitherto was thought to be based on a network of SiO_4 tetrahedra in which each tetrahedron shares at least three of its cor-

*We refer in this paper to "stable" glasses in the sense of glasses which can be obtained in gram quantities without crystallization and not in the sense of chemical resistivity.

ners with other tetrahedra. Exceptions to this condition were found only in glasses which contain cations of the non-noble gas-type such as Pb^{++} ions. However, recently J. M. Stevels and associates[11] developed a group of silicate glasses which were more basic than metasilicates in spite of containing only cations of the noble gas-type. In these glasses which he called "invert glasses," the average SiO_4 tetrahedron shares less than two of its corners with other tetrahedra.

The time has come, therefore, when one should reexamine current ideas on glass formation, especially the rules of W. H. Zachariasen[12] which have been used most widely, and find out more about the scientific basis of these ideas.

II. FACTORS CONSIDERED IMPORTANT FOR GLASS FORMATION

At the beginning of this century the work of G. Tammann[13] and his school provided a basis for discussing the physical chemistry of the glassy state. The most significant difference which exists between crystals and glasses is the effect which the past history of a glass has upon its properties. In contrast to crystals and to supercooled liquids, glasses were found to have physical and chemical properties which are not uniquely defined by their composition, temperature, and pressure, but which in addition to these parameters depended to a high degree on their previous thermal and pressure history. The resulting phenomena, especially the effect of the thermal history, are important both from a technical as well as a purely scientific point of view. Here a fundamental difference was discovered which led to the suggestion that the glassy state should be called a fourth state of matter which is governed by its own laws. The first questions which arose with respect to the glassy state concerned the causes of glass formation and the conditions which a substance had to meet in order to be transformable into a glass. This question has not yet been answered in spite of the many diversified approaches which were used in the last 30 years.

A second question which arose with the physical-chemical treatment of the glassy state concerns the remarkable similarity of properties such as thermal expansion or viscosity as functions of the temperature. The fact that some of the fundamental properties of the glassy state are common to vitreous phenolphthalein, selenium, and alkali silicates poses a fundamental problem which should no longer be ignored because its solution must provide a key to the glassy state.

The work of Abbe and Schott on the development of new optical glasses seemed to establish the fact that the formation of a glass is restricted to those oxides which form acids with water, namely SiO_2, B_2O_3 and P_2O_5. How can one link acidity to glass formation? The work of Tammann[13] showed that many substances which would be called basic from a chemical point of view, e.g., brucin, do form glasses readily. Others which are neutral from the viewpoint of aqueous chemistry, e.g., selenium and salol, were found also to be excellent glass formers.

Now we shall briefly discuss the factors which in the course of time were suggested as instrumental in glass formation.

1. The Shape of Molecules

During the seventeenth century great discoveries and advances were made in the field of mechanics by Newton, Kepler and other outstanding scientists. It was only afterwards that chemistry developed into a science so that it is not surprising that mechanical concepts influenced the thinking of chemists at an early stage. It was only natural to look for mechanical explanations for the forces which are active in the molecules and even for some specific properties of substances. In the seventeenth century French chemists attributed the biting taste of acids and their ability to corrode metals to the pointed shapes of their molecules. The sharp pointed molecules, it was thought, bore mechanically into the cavities of metals and destroyed them.

Exact knowledge of the shape of molecules became available only recently; hence, scientists had to speculate on the shapes of molecules and these speculations were based on the properties of substances. It was again natural to look for mechanical concepts which could account for the failure of a liquid to crystallize. Hence, glass formation was associated with the odd shapes of molecules.

The ability of a substance to polymerize and form chains was one of the most widely accepted prerequisites of glass formation. Firstly, some organic high polymers which consist of long carbon chains have viscosities and transformation temperatures analogous to inorganic glasses. Secondly, the existence of chain structures could be proven for some inorganic glasses, in particular elemental sulfur and selenium, and a group of phosphate glasses. Chain structures are quite common in crystalline silicates and there is no reason to exclude the possibility of silica chains participating in silicate glasses. The original concept of R. B. Sosman[14] (1922) that vitreous silica contains silicon chains analogous to the carbon chains in organic polymers could not be maintained. Vitreous silica is definitely not built up from chain molecules but must be considered to be essentially a three dimensional polymer which is not very different from cristobalite except that it lacks its periodicity and long range order.

Elemental sulfur owes its ability to form a glass to the shape of its molecules. Molten sulfur just above the melting point consists of ring-shaped molecules of the formula S_8. This liquid does not form a glass on chilling. At higher temperature the molecular structure of liquid sulfur undergoes a change which leads to the formation of high polymer chains. In this molecular state the liquid can be chilled to a glass.

Some chainlike organic molecules, e.g., stearic acid, crystallize readily if their melts are cooled; therefore,

one cannot assume that anisodimensional molecules are more likely to form glasses than others.

G. Hägg[15] (1935) emphasizes that glass formation must be caused by some characteristic features of the constituents of the melt. Without singling out chains in particular, he speaks of large groups which had irregular shapes. These groups of associated molecules were thought to have a certain stability because the atoms within the groups were held together by forces which were strong as compared with those acting between the groups. For many years the occurrence of macromolecules of irregular shapes and weight and the presence of association and disassociation products of simple and complex compounds (silicates, borosilicates, etc.) was used for explaining the properties of glasses as affected by their compositions and their previous history. The complexity of these melts was cited also as a reason for glass formation itself.

The concept that chains become entangled in a liquid and prevent glass formation is a strictly mechanical picture which is gradually being replaced by one which involves forces. The irregularity of a group must not necessarily be vested in its shape but can well be the result of its force field. When A. Dietzel and E. Deeg[16] experimented with glass formation using mechanical models representing silicon and oxygen ions, they substituted magnetic forces for the electrical forces. The formation of SiO_4 groups could be demonstrated with a set of magnets floating on water in a basin. The individual "ions" were round and the ratio of their sizes corresponded to that of the sizes of Si^{4+} and O^{2-} ions. Such a model system, when given the necessary mobility, "crystallized" but did not form a glass. In order to induce glass-forming properties into the mechanical model, it was not necessary to change the shape of the "ions"; it was sufficient to introduce an asymmetry into their force fields by moving the individual magnets out of their central positions.

Today when scientists talk about chain structure in glass they think much more in terms of the distributions of binding forces than of the shape of molecules, i.e., aggregates of atoms which have a high degree of permanency in the melt. Thus J. B. Murgatroyd[17] (1948) in his work on the delayed elasticity of glass fibers assumed the formation of chains; however, he speaks of the orientation of weak and strong bonds during the drawing process. As the bonds are electrical in nature the original mechanical concept is being replaced by one which is electrical and which considers forces rather than shapes.

When we look at the pictures which Tammann[13] used for explaining the effects of pressure on the properties of glasses by the "bending" of molecules during compacting and their "straightening out" on heating, we should interpret their shapes in terms of forces and electrical symmetries. The concept of "bent molecules" has disappeared in the current literature and has been replaced by that of "bent bonds" or "changed bond angle".

As the situation presents itself today we know inorganic glasses which consist of real molecular chains in the classical sense (sulfur, selenium) and others which contain chainlike arrangements of polyhedra in very much the same fashion as they occur in crystals (phosphate glasses).

The formation of strongly anisodimensional particles presents a fascinating problem in itself but nobody has yet been able to answer the questions: Why does the reduction of solid Ag_2S or CuBr vapor by hydrogen gas produce metallic silver and copper in the form of "hairs"? Why does the condensation of silica around places where silica glass is blown or drawn lead to a condensation of SiO_2 which has the form of spider webs? There are many examples of chain formation in systems which are not described as consisting of molecules.

2. The Nature of the Chemical Bond

Three kinds of forces are known to us: electrical, magnetic, and gravitational forces. In glasses we can ignore the gravitational and the magnetic forces and regard the binding forces as electrical in nature. The electrical interactions which are responsible for the formation of the condensed state have been grouped into several types, and one speaks of van der Waals' metallic, ionic, and covalent bonds. As far as these bond types are concerned we are sure that the metallic bond is not conducive to glass formation. Some molten metals, especially those of the iron and platinum group, can be supercooled to a considerable degree, but true metals always crystallize.

The van der Waals' forces are considered weak, but they increase with increasing number of electrons within the particles. Fluorocarbons have a higher temperature coefficient of viscosity than the analogous hydrocarbons so that some fluorocarbons can be obtained as glasses at low temperature. In this case the solidification of the liquid is due to van der Waals' forces in the purest form.

Van der Waals' forces are also active in the condensation and crystallization of molecules such as benzene and naphthalene, but typical glass-forming organic substances, e.g., sugar, glycerol, alkaloids, etc., contain functional groups which permit hydrogen bonding. Hydrogen bonding is responsible for glass formation of aqueous solutions.

The bonds within the molecules of an element are called "covalent". The atoms in the chlorine molecule Cl_2 are described as being bonded by an electron pair which is shared between the two Cl atoms. This type of chemical binding is the prototype of the covalent bond which exists in its purest form only between atoms of the same kind such as the carbon atoms in a hydrocarbon.

The elements which can form glasses are oxygen, sulfur, selenium, and perhaps tellurium. These elements are unique inasmuch as they can form paramagnetic molecules which contain two unpaired electrons. As a rule, a stable molecule contains an even number of electrons and this rule has only a few exceptions. Thus the

molecule NO contains an odd number of electrons and a molecule which contains an unpaired electron is paramagnetic and it can dimerize. As a result of its dimerization the paramagnetic NO forms diamagnetic N_2O_2 at low temperature.

The oxygen molecule, O_2 has two unpaired electrons which enables it to dimerize but also to form chains of greater length. The dimer of O_2, i.e., the molecule O_4, has been discovered in the atmosphere by O. R. Wulf[18] (1938). Applying the K. Fajans'[19] quanticule formulation to the molecule of oxygen, one can understand the reason for its polymerization. According to Fajans the O_2 molecule consists of two oxygen cores O^{6+} which are held together by ten electrons which are quantized with respect to both cores. The two unpaired electrons are quantized with respect to only one O^{6+} core each:

$$e^- \; O^{6+} \; (e^-_{10}) \; O^{6+} \; e^-$$

The energy gain through the pairing of two single electrons is very small so that polymerization is negligible at ordinary temperature. At low temperature, however, dimerization and polymerization becomes possible, and W. Wahl[20] (1913) claimed to have observed a high viscosity and even glass formation for elemental oxygen at low temperatures.

E. J. Shaw and T. E. Phipps[21] (1931) found that sulfur vapor is also paramagnetic, a result which was to be expected because it was known from spectroscopic data that in their ground states the molecules S_2 and O_2 are similar. At ordinary temperature the sulfur forms ring shaped S_8 molecules in which all electrons are paired. When these rings break open thermally they can form polymers of high molecular weight by sharing their unpaired electrons.

The sharing of unpaired electrons and the formation of oxygen and sulfur polymers is a unique process which is distinctly different from the formation of oxide and sulfide glasses. It may be a mere coincidence that among the very few elements which can form glasses one finds oxygen, which is also the most important constituent of technical glasses.

Elemental selenium differs from sulfur only inasmuch as in the crystalline selenium infinite chains of selenium atoms are already present so that the molecular structure of selenium does not have to undergo the drastic change during melting as does elemental sulfur. Conventionally one treats the bonds in a sulfur or selenium glass as covalent within the chains and the electrically neutral chains are held together by van der Waals' forces.

The "ionic bond" is the bond type that is active between particles which differ very much in their affinity for electrons, e.g., between Na and F atoms. These atoms interact in a way which can be described as the complete removal of an electron from the sodium atom and the completion of an octet shell of the fluorine atom. This electron transfer leads to charged particles, namely, the positive sodium ions and the negative fluorine ions. These charged particles can interact further by forming a condensed system in which they are held together primarily by Coulomb attractive forces. The ionic bond is active in fluoride glasses, e.g., in the alkali beryllium fluoride glasses which first were studied by G. Heyne[22].

The glass-forming compounds discussed so far represent the different bond types in their purest form. If atoms are not identical as in glassy selenium but are not quite as different as sodium and fluorine atoms, in NaF, they are conventionally treated as forming "mixed bonds". L. Pauling[23] calls the binding forces in silica, 50 per cent ionic and 50 per cent covalent. The degree of covalency of a bond is expressed by the "electronegativity" of the atoms. The greater the value of the electronegativity of an element, the more covalent is its bond to oxygen.

The bonds in vitreous As_2S_3 are considered more covalent than those in SiO_2 and the bonds in vitreous $ZnCl_2$, BeF_2, in the complex alkali beryllium fluoride, and in the alkali calcium nitrate glasses are considered more ionic.

J. E. Stanworth[24] introduced the electronegativity of the elements, i.e., the tendency of a neutral atom within a molecule to attract electrons, as a parameter which might be linked to glass formation. J. M. Stevels[25] suggested a subdivision of elements into four groups (Table I). The first group comprises the "real glass formers" and the second group the "probable glass formers". The third group comprises those elements whose oxides cannot form glasses but their effect upon the density of glasses reveals a stronger interaction with the network than that of the oxides of the elements of the fourth group.

Table I

ELECTRONEGATIVITY OF ELEMENTS AND ROLE IN GLASS STRUCTURE*

Real Glass Formers		Probable Glass Formers		Metallic Ions Contracted Glasses		Which Form Normal Glasses	
P	2.1	Sn	1.7	Be	1.5	Ca	1.0
B	2.0	Ti	1.6	Mg	1.2	Sr	1.0
As	2.0	Zr	1.6	Li	1.0	Ba	0.9
Si	1.8	Al	1.5			Na	0.9
Ge	1.8					K	0.8
Sb	1.8					Rb	0.8
						Cs	0.7

*After J. M. Stevels

Table I reveals that those elements whose atoms have a low electronegativity (i.e., those which form basic oxides) are not potential glass formers. However, as far as the elements with high electronegativities are concerned, no such relation exists between their ability to form a stable glass and the value of the electronegativity of the atoms. Antimony has the same electronegativity as silicon but its oxide does not form a stable glass. The aluminum atom has a lower electronegativity than the tin atom or the zirconium atom but alkaline earth aluminate glasses are known, whereas no vitreous zirconate or stannate has been reported.

When A. G. Smekal[26] (1951) discussed his views on

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62nd A.C.S. Annual Meeting

GLASS DIVISION PAPERS *(conclusion)*

Investigation of Structure in Lead Borate Glasses.

By Robert L. Hallse,
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and *Ralph L. Cook,*
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS.
Presented by Mr. Hallse

Five lead borate glasses ranging in composition from 25 to 65 mol per cent PbO, with the remainder being B_2O_3, were studied in order to determine their structure. The investigation was carried out in two parts:

1. Correlation of experimental and calculated X-ray intensity curves.
2. Determination of various physical properties of the glasses.

The X-ray work consisted of obtaining X-ray diffraction patterns of the glasses using an X-ray diffraction powder camera, converting these patterns to X-ray intensity curves by means of a microphotometer, and finally plotting X-ray intensity versus sin θ/λ. The samples used in the X-ray camera were thin films of glass which were fragments of bubbles which had been blown from the glasses. X-ray exposure times were one-half hour using a copper tube operated at 15 milliamps and 40 kilovolts.

These experimental intensity curves were then compared with curves obtained by first assuming a structure for the glass and then calculating the X-ray intensity at various values of θ that would result from the assumed structure. This was done using an equation having the form:

$$I = \sum_m \sum_n f_m f_n \frac{\sin sr_{mn}}{sr_{mn}}$$

where $f_m f_n$ = atomic scattering factors for m and n atoms, respectively

$$s = \frac{4\pi \sin\theta}{\lambda}$$

r_{mn} = distance between m and n atoms

The assumed structure was modified until good agreement resulted between the experimental and calculated intensity curves. It was concluded from the X-ray evidence that lead borate glasses in the composition range studied consist of a random network of BO_4 tetrahedra, with lead atoms having a coordination number of six occupying holes in the structure. Short range order was thought to exist with definite interatomic distances extending to 6.7 A, this being the distance between two lead atoms.

It was thought that if such a random network did exist a plot of any physical properties versus the percentage of one component in the glass would result in smooth curves, and that any maxima or minima in the curves would indicate a change in the coordination number of the boron or lead atoms, or the formation of a compound.

The properties determined were coefficient of thermal expansion, softening temperature, transition temperature, index of refraction and volatility. Density and surface tension data obtained by other investigators were also studied. All properties except volatility, surface tension and composition of the volatilized vapor indicated a random network structure. The surface tension and lead content of the volatilized vapor both reached their maximum values around 82 per cent PbO and the volatility curve had a minimum in this same region. Since the surface tension data were obtained at 900°C. and the volatility data obtained at 1100°C., it was concluded that at elevated temperatures the compound 5 $PbO.4B_2O_3$ tends to form.

Constitution of Mixed Alkali Cation Phosphate Glasses.

By M. Krishna Murthy and *A. E. R. Westman,*
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and *M. Joyce Smith,*
FORMERLY RESEARCH FELLOW, ONTARIO RESEARCH FOUNDATION.
Presented by Mr. Murthy

The method of analyzing phosphate mixtures by the paper chromatographic technique, perfected by the Ontario Research Foundation, was applied to a study of the con-

stitution of water-soluble alkali phosphate glasses. Previous investigations had shown that these glasses contained various phosphate anion groups, both linear and cyclic polymers with the exception of orthophosphate, and that their distribution was a function of phosphorus/cation ratio. In the previous studies, however, experimental difficulties encountered in the quenching of the melts into glass had prevented a detailed study of glasses with M_2O/P_2O_5 ratio greater than 1.66 and n (the number average chain length) less than 3.

It has now been ascertained that the limit of glass formation can be extended towards higher alkali ratios by using a mixture of alkali cations instead of a single alkali cation. Glasses with constant lithium but widely varying Na-K ratios (Li:Na:K:: 1:1:5; 1:2:4; 1:3:3; 1:4:2; 1:5:1) were prepared with n value varying from 2.25 to 9. In miscellaneous compositions studied, it was possible to prepare glasses with n value as low as 1.5.

Results of chromatographic analyses of mixed cation glasses demonstrated that the distribution of phosphorus between various polymers was almost the same as for sodium phosphate glasses and was independent of the ratio of alkali cations present. Contrary to the theory of Van Wazer, glasses with n value of 1.5 and 2 contained a considerable amount of orthophosphate.

Glass Formation in the System Arsenic-Sulfur-Bromine.

By A. David Pearson and *William R. Northover,*
BELL TELEPHONE LABORATORIES, MURRAY HILL, NEW JERSEY.
Presented by Mr. Pearson

A new series of inorganic glass compositions, some of which are liquid at room temperature, were described by Mr. Pearson. These glasses are composed of varying proportions of the elements arsenic, sulfur, and bromine.

The new tenary compositions with bromine show even lower softening and high-fluidity temperatures, with several as fluid as glycerine at room temperature. In spite of this, they are glassy solids at lower temperatures, show conchoidal fracture like typical silicate glasses, and exhibit no extensive ordering in their structure.

Wide ranges of softening points and chemical compositions can be achieved. For example, substantial amounts of bromine (up to 20 per cent) can be used in the ternary mixture without dropping the softening temperature. With the addition of greater amounts, softening and high-fluidity temperatures decrease to room temperature and below.

Another interesting aspect of the new glasses lies in their optical transmission properties. They are all transparent, ranging in color from ruby red to light amber. The indexes of refraction appear to range between 1.9 and 2.0, which is comparatively high for glasses.

Preparative techniques are relatively simple. The measured amounts of each of the constituents are weighed into a quartz tube with a pulled-down neck. The contents are then frozen in liquid nitrogen, the tube evacuated and sealed off. These sealed tubes or ampules are then encased in a simple pipe-bomb, and heated in an oven at about 400°C for three to four hours. Simple agitation is sufficient to bring about reaction in the cases where glass formation occurs. The rate of cooling to room temperature does not appear to be critical.

Outside the area of glass formation in the phase diagram, crystalline materials are formed, or else the compositions precipitate sulfur. However, within a large area of composition variation, glasses show no tendency toward instability over extended periods of time.

Previous work at Bell Laboratories on compositions of arsenic, sulfur (or selenium), and thallium produced glasses which softened somewhat above room temperature, and became fluid enough to use for dip-coating at temperatures between 125 and 350°C. The new compositions as shown in this paper, however, appear to show the same characteristics. They are relatively stable toward acids, but are attacked by alkalis. They tend to hydrolize in water, with this tendency increasing in compounds showing lower softening points. The solids show good bulk resistivities, with values as high as 10^{15} ohm-cm. The resistivities of the liquid compositions are not as high, lying around 10^{9} ohm-cm.

The Dual Role of Niobium in the System SiO_2·K_2O·Nb_2O_5.

By Bh. V. Janakirama Rao,
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Area of glass formation in the system $SiO_2.K_2O.Nb_2O_5$ was indicated. The properties of glasses in the system were determined and studied. Density, refractive index, molar refraction, and dielectric constant increased with increasing molar additions of Nb_2O_5. Chemical durability, coefficient of expansion and softening temperature curves indicated transitions. It was postulated that Nb^{+5} ion plays a dual role as a network modifier and as a network former in the system.

SYMPOSIUM ON HEAT TRANSFER

Chairman: Clarence L. Babcock, Owens-Illinois Technical Center.

It was pointed out by Mr. Babcock that the transfer of heat through glass is of major importance, from ordinary temperatures up through its entire melting range that might extend possibly as high as 1500°C Considerable amounts of heat are used in melting and producing the glass initially, and glass acts as a transferring medium or barrier depending upon its use. It was quite appropriate to invite leaders in the field of investigation of heat conductivity processes to take part in this symposium, and nine papers by well-known investigators from the United States, England, Belgium, and France were presented. The first two papers were primarily concerned with a summary and historical presentation of the applications and importance of the various processes used, and the remaining papers were devoted to specific methods of experimental research.

Heat Conductivity Processes in Glass.

By W. D. Kingery,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS.

This paper discussed the phonon conduction process or "true" thermal conductivity of glass. The thermal conductivity of glass is important for many applications. It determines the temperature gradient that is set up under a fixed heat flow, and, as a result, is one of the determinative characteristics fixing the thermal stress resistance of glass products. The heat transfer properties are also of great importance in glass forming. This is true for melting, annealing, and forming on automatic glass forming machinery. In addition to practical applications, thermal conductivity measurements may prove to be a useful tool in the elucidation of glass structure and the study of the vitreous state.

Two main processes account for heat conduction in glass. At low temperatures the major process corresponds to energy transfer via thermoelastic waves. The thermal conductivity resulting from this process is low as a result of strong scattering by the random structure. At high temperatures this conduction process is overshadowed by radiation heat transfer processes.

A Review of Radiant Heat Transfer in Glass.

By Robert Gardon,
PITTSBURGH PLATE GLASS COMPANY, PITTSBURGH, PENNSYLVANIA.

The purpose of this paper was to present a brief review of recent work on the topic of heat transfer, along with a discussion of the relationship of this work to current industry problems. Written in a non-mathematical manner, the paper was directed primarily toward an elucidation of the underlying physical phenomena. It considered, first, the absorption of radiation by semi-transparent materials; second, the emission of radiation from semi-transparent bodies, as it is affected by the interaction of internal emission and absorption; and, third, the mechanism of internal energy transfer brought into being by this interaction sometimes called "radiative conduction."

Underlying the considerations of this paper was the fact that in diathermanous materials both the absorption and emission of radiation are bulk phenomena. The interaction of these phenomena determines the net rate of emission of radiation from diathermanous bodies and gives rise to a mechanism of heat transfer that entails, not the familiar radiation through the bodies, but a process of radiant exchanges between nearby layers. In the deep interior of diathermanous bodies this mechanism resembles thermal conduction; therefore, it has been described by an equivalent "radiative conductivity." For glasses at elevated temperatures this "radiative conductivity" is far greater than the true conductivity. The utility of this concept is limited, however, by its inapplicability near boundaries. The "apparent conductivity" of glass objects of moderate thickness is a true physical property, for it depends not only on the material and its temperature but also on the thickness of the body in question and on the process to which it is being subjected.

Although the basic phenomena involved in radiant heat transfer are well understood, mathematical formulation of the problem is so complex that solutions have, as yet, been found for only the simplest geometries. From the point of view of practical glass technologists even some of these "solutions" are too complicated, and the search continues for simpler representations and further simplifications applicable to specific problems. Many of the physical parameters that may be involved have not yet been adequately determined. An example is the true thermal conductivity of glasses at elevated temperatures, which is important in processes involving thin layers of glass and rapid rates of quenching. Another major remaining problem is that of temperature measurements in hot glass. Finally, there is the ever-present challenge of fruitfully applying the findings of research, either theoretical or experimental, to the technological problems of the glass industry.

Determination of the Spectral Transmission of Glass in the Temperature Range from 20°C to 1400°C and Application of the Results to Heat Transfer Problems and to Techniques of Temperature Measurement.

By H. Charnock, F. J. Grove, and J. R. Beattie,
PILKINGTON BROTHERS, LTD., ST. HELENS, ENGLAND.
Presented by the authors in three parts.

In the processes of glass melting, fining, forming, and heat treating, accurate knowledge and control of temperature conditions are very important. At the temperatures involved, practical and theoretical approaches to the problems of measurement or control were required to assess the contributions from the various mechanisms of heat transfer in the determination of overall temperature distributions. In particular, because glass is semi-transparent, the role of thermal radiation must be considered; hence a knowledge of the absorption coefficient of glass as a function of wavelength and temperature was a fundamental prerequisite. This basic information was then applied

1. In the field of the steady state temperature distributions in glass tank furnaces, where a formal solution of the heat transfer equation is available;
2. To the possibility of using this formal solution to describe a periodic temperature change;
3. To the measurement of temperature distributions in flat plates during annealing or toughening processes.

The apparatus used for the measurement of spectral transmission of glass at high temperatures was first described by Grove and Jellyman in 1955. The modulated radiation from the globar source was first focused on the sample in the center of the furnace, and then on the entrance slit of the monochromator.

At temperatures above the softening point, the glass was contained in a cell consisting of a platinum-rhodium vessel with two synthetic sapphire windows, 1 inch

square, cemented into position parallel to each other and ¼ inch apart. The cement was fired in an auxiliary furnace and the cell filled with glass, while hot, by tipping it slightly and allowing small pieces of glass to melt on the incline formed by the side of the cell. This procedure was adopted to avoid trapping air bubbles in the sample. The cell was then transferred to the main furnace without being allowed to cool.

Suitable corrections were applied for the absorption and reflection losses of the sapphire windows.

Practical experience in the manufacture of glass has shown, in a general way, that glasses which have a different color usually must be melted in furnaces of different depths. The work reported in this paper showed theoretically how these differences may be predicted and how the temperature gradients and bottom surface temperatures in a commercial tank melting furnace may be calculated.

The theoretical steady state radiation conductivity may be used to describe the temperature conditions resulting from the application of a periodic temperature change to a large volume of glass, provided the amplitude and frequency of the temperature oscillation are sufficiently small. Because these conditions were reasonably fulfilled at the higher temperatures in the experimental work described, the discrepancy between the theoretical and measured values was attributed to experimental error. The general equations presented provided a basis for testing the validity of the assumption that the steady state radiation conductivity may be used to describe any transient temperature change.

Cooling of Window Glass and Temperature Measurement by Radiation Analysis.

By R. Van Laethem, L. Leger, M. Boffe, and E. Plumat,
UNION DES VERRERIES MECANIQUES BELGES, CHARLEROI, BELGIUM.
Presented by Mr. Plumat.

This paper was a continuation of the study of determining temperature distribution in glass flow. Peyche's, Genzel's, Czeny's and Gordon's researches were used as an aid in the theoretical study of the radiant emission of a glass volume through its surface. From a theoretical study of the cooling of a horizontal flow of glass, the authors established the quantitative relationships between the spectral composition of the emitted radiation and the vertical temperature distribution. The paper proved the possibility, under certain conditions, of measuring the surface temperature and the temperature repartition characteristics by means of a set of several optical receptors.

The experimental work consisted of analyzing the radiant heat transmission in glass at different temperatures. The apparatus used permitted the measurement of heat transmission in glass and the separation of the radiation and convection effects. The thermal flux intensities were measured either by a calorimetric method or by monochromatic optical pyrometry.

The apparatus permitted the reproduction of different types of heat transmission and emission through variable glass thicknesses and the variation of the principal radiation parameters including the emissivity of the supporting glass.

As a conclusion, some practical results obtained by measuring glass temperatures in actual industrial furnaces by special optical pyrometers were presented. However, more complete results will be presented later.

Overall Heat Transmission Coefficients of Amber and Green Glasses in Temperatures of the Melting Range.

By S. Kruszewski,
UNITED GLASS, LTD., CHARLTON, ENGLAND.
Presented by H. H. Holscher, Owens-Illinois Technical Center, Toledo, Ohio, in the absence of Mr. Kruszewski.

Over the years certain empirical data concerning glass color and heat transfer have been developed. The purpose of this practical paper was to substantiate certain of these data. A simple laboratory technique was devised to measure Rodnikova's "apparent conductivity" (known as the total heat transmission coefficient) which is the sum of the "radiation conductivity" (the true thermal conductivity) and the heat transfer by convection. The latter was negligible under the conditions of the experiments described in this paper.

The heat transmission data collected for a number of colored glasses were then used in reviewing the design of existing tank furnaces. An attempt was also made to determine the effect of various coloring oxides on the heat transmission through green glass.

A gas fired, laboratory furnace was built to a design which insured a considerable downward heat flow through the glass, while heat flow in a horizontal direction was minimized by means of insulation.

The furnace was used to investigate the effect of chromium oxide, nickel oxide and iron oxide on the overall heat transmission coefficient of green glasses. An empirical equation was derived, relating heat transmission coefficient to concentration of coloring oxides.

It was concluded that:

1. A total heat transmission coefficient of a glass may be determined by a simple method, which does not require any expensive equipment. The results obtained are accurate enough for practical purposes of furnace design or for deciding on the choice and concentration of the coloring agents used in melting of a colored (green) glass. This method, which gives only a mean coefficient for a range of temperatures would not be accurate enough for academic research.
2. Light transmission of amber glasses in the near infrared measured at room temperature appeared to give a useful indication of their relative heat transmission properties in a furnace.
3. A significant correlation was found between the total heat transmission coefficient and concentration of coloring oxides in green glasses. An empirical equation was derived, which showed that the nickel oxide is 7 times as powerful as iron oxide and 3 times as powerful as chromium oxide in its effect on the heat transmission coefficient.

4. Glass temperatures at the bottom of commercial tanks may be calculated for a given glass depth and bottom construction, including insulation. The agreement between true and calculated bottom glass temperatures was better for colored glasses than for a colorless glass. In the latter instance heat transfer to the bottom of a tank was markedly affected by convection currents.

Tuesday Afternoon

Temperature Distribution of Glass in Blank Molds of Hollow Glass Machines.

By W. Trier,

HUTTENTECHNISCHE VEREINIGUNG DER DEUTSCHEN GLASINDUSTRIE, FRANKFURT AM MAIN, WEST GERMANY.

This paper described a new apparatus that makes possible the study of the axial flow of glass in cylindrical molds under defined conditions. From the figures of flow, the differences of viscosity in glass may be deduced. When these flow experiments were combined with a temperature measurement, the radial viscosity and temperature distribution in glass could be determined.

The profiles of temperature calculated by this method, which showed clearly the progressive cooling of the glass from outside to inside, were discussed. As expected, the cooling curves of green glass differed markedly from those of flint glass. From the temperature distribution it is possible to determine the local course of heat flow in glass and the change with time, especially in the zones near the border.

Relations Between Heat Losses of Glass, Forming Times, and Bottle Production in Blowing Machines.

By W. Giegerich,

GLASHUTTE HEILBRONN A.G., HEILBRONN, WEST GERMANY.

Presented by Mr. Trier in the absence of Mr. Giegerich.

The author emphasized that in many areas our empirical knowledge has far outstripped our technical and scientific knowledge. Many times difficulties arise for which there is apparently no solution. For example, critical judgment of the capacities and the forming times of various glass processing machines is a task that must be performed currently, almost daily, in glass works because it is closely related to the necessity of ascertaining the best way of operating such machines. An exact technic-scientific evaluation of the forming times is hardly possible for the following reasons:

1. The presently meager knowledge of heat transfer and flow during formation.
2. The great, nearly insurmountable difficulties with respect to the technical problems of measurement.
3. The variety of the manifold operational influences.

Therefore the author attempted to describe in simple terms the chronological sequence of the individual operations of the forming process and the cooling of the glass during this process. On the basis of exact time studies of the individual operations, and with the aid of many calorimetric measurements of the heat rates in the individual forming stages (made on numerous full-automatic blowing machines) the author presented—by means of classification and comparison of the above mentioned findings—approximate operational values.

The Transfer of Heat in Glass During Forming.

By D. A. McGraw,

OWENS-ILLINOIS TECHNICAL CENTER, TOLEDO, OHIO.

Fewer than 20 years ago, there were many adherents to the theory that radiation was not an important contributing factor in the transfer of heat in melters. The argument was based on the fact that direct radiation is absorbed in a few inches of glass depth. It was reasoned that it was impossible for perceptible amounts of radiation to penetrate the depth of 3 or 4 feet of glass in a commercial tank.

The most lucid refutation of this idea, together with a qualitative explanation of radiative exchange within the medium, was made by Preston in 1947. It was followed by the theoretical treatments of Kellett and Czerney and Genzel, who almost simultaneously presented the concept of a radiation conductivity. This concept applies to glass of great thickness, under steady-state conditions of heat transfer; it has led to a fine series of theoretical developments, all relating to radiation transfer in the glass tank.

There still remained unexplained, however, the behavior of heat transfer under transient conditions, in relatively thin layers of material. This is the problem encountered in forming, annealing, and tempering of ware. The solution of transient heat transfer problems is difficult even when conduction is the only mode of transfer. When an investigator compounds the task by including the contributions of radiation transfer and takes account of the refractions and multiple reflections occurring in a thin layer, the exercise becomes one of almost staggering complexity.

Because of these difficulties, the theoretical approach was virtually untouched until Gardon's papers were presented. He solved the problem explicity for the heating and cooling of glass sheets, as in annealing and tempering. The background theory for radiation transfer during forming is also implicit in his treatment; only changes of boundary conditions are required to make a direct application.

During the forming of glass ware (pressing and blowing operations) radiation contributes little to the temperature distribution within the glass. The net heat transfer is almost 100 per cent by conduction. Glasses that differ in infrared absorption characteristics, but are otherwise the same in physical properties, should behave similarly in these phases of operation.

After forming, and during the long-term reheat that occurs on the conveyor, the role of radiation transfer inside the glass increases somewhat in importance. Differences in radiation properties among glass compositions should have their greatest effect at this time. Long term reheat should be slower in iron-colored glasses (such as amber) than in flint glass; hence slightly higher production rates should be possible with colored glasses. In actual practice, however, the total effect is quite small, and is too uncertain, job to job, to consider color as a factor in setting production goals.

Proceeding from the principle that the important process is conduction, this paper pointed out that the general course of the thermal conductivity-temperature curve for container glass has been established for the forming range, 1200°F to 2000°F. The conductivity increased from 14 to approximately 18.5 Btu-ft.$^{-2}$-hr.$^{-1}$in^{1}-°F^{-1} between these temperatures.

It was also found that the rate of removal of heat from ware was greatly influenced by the behavior of the glass-to-mold heat transfer coefficient during the period of contact. In a typical parison pressing operation the coefficient had a value of more than 2000 Btu-ft.$^{-2}$-hr^{-1}-°F^{-1} at first contact, but decreased rapidly to about 500 Btu-ft.$^{-2}$hr.$^{-1}$-°F^{-1} at the end of a 1.4 second dwell period. To obtain best advantage of the high initial value, it was important to obtain full glass-to-mold contact as fast as possible, as well as maintaining pressure in the first part of the dwell period.

These phenomena, i.e., variable thermal conductivity and variable interface coefficient, characterized the process of heat extraction during most forming processes. If, however, the glass thickness is greater than ½ inch and the glass cooled at a slow rate, the contribution of radiation transfer must also be included. Further forming data are needed relating the effects of such variables as dwell time, contact pressure, and mold surface condition on the interface coefficient; in particular, a detailed study of a blowing process is needed. By the utilization of empirical data on these variables in the computing methods now available, the heat transfer problems of forming may be calculated (for the first time) on a completely quantitative basis.

An Estimation of the Heat Transfer Conditions in Glass by Cinematography of Strains During Heat Treatment.

By P. Acloque,

CIE DE SAINT GOBAIN, PARIS, FRANCE.

When samples of glass were observed through a fringe polariscopic device during heat treatment, it was possible to see the deformation of the fringe pattern owing to the strain evolution. Cinematographic recording of this evolution made it possible to obtain information about the heat transfer conditions in a glass when exposed to cooling or heating by convection processes, especially when the temperature distribution was such that some parts of the glass were above and others below the strain point. Therefore, between the 2 parts, a "strain-front" did exist, and the propagation of this strain-front materialized the diffusion of a given temperature.

Two short-length films were presented and interpreted. The object of the paper was to show how it is possible to analyze photoelastic motion pictures of glass samples in order to deduce from the strain patterns the thermal behavior corresponding to the treatments undergone by the samples. The apparatus was described, and two cases were considered. The first one, dealing with tempering, showed that information can be gained from the films in regard to the so-called "devitrification temperature" on the one hand and the external heat transfer coefficient on the other. The second film illustrated the treatment of Temnization.

The two cases considered showed that, although the size of the samples and the simplifications used for solving the mathematical problems involve some limitations, it is possible to draw valuable information in heat transfer phenomena from the chromophotographic analysis of the setting of strains. Since the direct methods for measuring and recording temperature in the rapid treatments are neither easy nor accurate, especially inside the samples, it appeared that this method is of interest for measuring the heat transfer coefficients involved in the processes. The deduction of external heat transfer coefficients seemed particularly sound.

Wednesday Morning

Chairman, Frank R. Bacon, Owens-Illinois Technical Center, Toledo, Ohio.

Glass Fibers: General Contrasts in Low-Melting and High-Melting Forms Based on Composition.

By Alexander Silverman,

PROFESSOR EMERITUS, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA.

The paper dealt with the general characteristics of low-melting glass fibers in contrast with those of high-melting glass fibers. The differences discussed not only included the lower and higher melting temperatures but also the general characteristics of each of these two classes of fibers. In low-melting glass fibers, modifications made by introducing any one of a variety of chemicals changed not only the melting point and the physical properties but also the chemical properties. In the higher-melting glasses, there was a much higher series of melting points, but the properties of these glasses generally varied in a manner different from those of the low-melting glasses. These contrasts were so pronounced for the two types of fibers that an outline of their relative trends would prove most valuable for individuals interested in the field of glass fiber production and research.

An Analysis of Heat Flow in Soda Lime Glass.

By Julius J. Torok,

OWENS-ILLINOIS GLASS COMPANY, KIMBLE GLASS DIVISION, TOLEDO, OHIO.

Because computation of heat flow in glass requires that the conduction and radiation components be known for various temperatures and thicknesses of glass, published and available heat flow data were analyzed by simple methods of electrical networks to derive values for the conduction and radiation components. This method offered a simple, easily used means of determining the transmission of heat through clear lime glass at any temperature and thickness. The radiation component found varied more with temperature than would be expected from classical theory. Most, but not all, of this discrepancy was found to be caused by adsorption of all radiation below 2.75 microns.

(*Continued on page* 464)

Bibliography on Glass Structure

PART II

14. Herbert Schonborn

"Constitution of Glasses," Sprechsaal, 61 (6) 99-101; (7) 117-20 (1928); Cer. Abs. 606 (1928).

The thermal coefficient of expansion and the electrical conductivity were determined and data are given of glasses of various compositions which were quenched from different high temperatures. The correlation between the determined physical constants and the quenching temperatures permits the drawing of conclusions on the molecular constitution of the glasses. In addition, the contractions were measured which quenched rods of glass undergo at high temperatures. Interdependence of time and the temperature at which the tests were made are expressed by formulas. Phenomena of inertia noted in viscosity measurements are given.

15. W. E. S. Turner

The Constitution of Glass, Book published by Soc. of Glass Tech., Cer. Abs. 504 (1928).

This book is a collection of papers discussing constitution, viscosity, x-ray measurements and includes altogether twelve chapters.

16. G. L. Clark and C. R. Amberg

"X-Ray Investigation of Feldspar Glasses," J. Soc. Glass Tech., 13, 290-96 (1929); Chem. Abs. 24, 4130 (1930).

Solution of Na_2O and Al_2O_3 in silica. The SiO_2 molecule in SiO_2 glass appears to be 6.928 A. long and 2.52 A. wide. The molecules are arranged end to end in long chains grouped in small cybotactic bundles. The molecules are separated from each other by small gaps of 0.222 A.

17. J. T. Randall, H. P. Rooksby and B. S. Cooper

"Structure of Glasses: The Evidence of X-ray Diffractions," J. Soc. Glass Tech., 14, 219-29T (1930); Z. Krist. 75, 196-214 (1930); cf. C. A. 24, 4697 (1930).

Numerous glasses were subjected to x-ray analyses. With copper K-alpha radiation a single intense band at 4.3 A.U. was obtained with vitreous silica. The strongest band for alpha cristobalite occurs in almost the same position. Thus it appears that vitreous silica is composed of cristobalite crystallites, probably consisting of an average of 20 molecules each. Amorphous or precipitated silica gives almost the same pattern, indicating that the difference between the crystal and the amorphous or vitreous states is one of degree, not of kind. Aluminum and boron do not destroy the silica lattice, while the strongly electropositive elements, as Ca and Na, do. The densities of glasses, their melting, electrolytic, expansion and viscous properties are briefly considered in the light of crystal characteristics.

18. P. Lazarev and S. Liosnyanskaya

"The Structure of Chilled Glass," Compt. rend. acad. sci. U.R.S.S., Ser. A, 1929, 107-8; Chem. Zenir. I, 630 (1930).

The decrease in density of chilled glass was studied from the surface to the center. This was done by grinding away the surface and progressively measuring index and density.

19. A. Granger

"Glass," Ceram et verrerie, 497-9, 551-4, 607-10 (1930).

The crystal structure of glass and the arrangement molecules or molecular phenomena involved are discussed. The devitrification of glass is considered from a physical viewpoint. As a liquid and unstable equilibrium, certain conditions prevent its crystallization. For devitrification the mass must contain one or more centers of crystallization, and these centers must develop so as to imply an appreciable rapidity of the crystallization.

20. O. Knapp

"Constitution of Glass Based on the Laws of Solutions," J. Soc. Glass Tech., 15 (18) 140-52 (1931); Cer. Abs. 683 (1931).

The hypothesis of oxide constitution of glass is not sustained by experimental data, although the additive effect of oxides on many properties of glass can be traced. No linear relationship was found between solubility and constitution of Pb glasses as suggested by the monohexasilicate hypothesis of Keppeler. The hypothesis of the highest silicate formation satisfied these conditions: (a) glass is composed of silicates in which acid or basic oxides may be dissolved; (b) a definite relation exists between the consitution and the physical properties of the glass; (c) the component silicates of a given type of glass are definite in kind through the range of possible compositions. Thus Knapp considers glass as a genuine solution of silicates in which most often free SiO_2 is dissolved.

*This series will be completed next year. Reprints will be available at nominal cost, provided there is sufficient interest. Order from Reprint Dept., THE GLASS INDUSTRY, 55 West 42nd Street, New York 36, N.Y.

The optical constants, alkalinity, H_2SO_4 solubility value, weathering and tarnishing values are in linear relationship with the compositions of glasses expressed as the highest silicates.

21. G. Tamman

"Existence of Compounds in a Liquid Phase," Z. anorg. allgem. Chem., 199, 117 (1931).

22. W. H. Zachariasen

"The Atomic Arrangement in Glass," J. Am. Chem. Soc., 54, 3841-51 (1932).

The author gives a list of materials that would form glasses based on structural considerations.

23. W. Weyl and W. Eitel

"Constitution of Glass in the Light of Solvation Theory," Naturwissenschaften, 20 (22-24) 422-25 (1932).

All properties of glass, particularly heat content and energy can be explained from its constitution as a solution of the various constituents in each other, by taking into account their possible thermal and electrical dissociation and consequent electrical forces, the latter giving rise to solvation of the ions. The boric acid glasses with abnormal viscosities, "mineralizer" actions, etc., all can be considered from the same viewpoint. Study of these effects by means of the absorption spectrum of glasses with Ni added is described.

24.

Theories of the Constitution of Glass, anon., Rev. belge. Ind. verrieres, 2, 125-26 (1931).

25. W. Weyl

"Constitution of Glass I. Explanation of Glass Anomalies on the Basis of Dissociation and Solvation Phenomena," Glastech. Ber. 10, 541-56 (1932); Chem. Abs. 27, 2264 (1933).

A theoretical explanation is given of the so-called anomalies of the glassy state based on the theory of ionization and solvation by treating glasses as chemical solutions. In this way (1) energy content and specific heat, (2) stability of the glassy state, (3) vol.-isobars and vol. isotherms, and (4) viscosity of glasses are discussed.

26. B. G. Podolsky

"Constitution of Glass," Ukrainsky Silikaty, No. 11-12, 473-77, (1928); Cer. Abs. 11 (1933).

27. Lord Rayleigh

"Large Scale Crystalline Structure in Certain Glasses of Exceptional Composition," Proc. Roy. Soc., A137, 55-61 (1932); cf. C.A. 14, 327 (1932).

A number of glasses of unusual composition, when examined between crossed nicols, show a weak doubly-refractive, quasi-crystalline structure. This is found in highly siliceous glasses down to 80% SiO_2, and phosphatic glasses such as "Corex" and in boracic glasses. This structure is not due to faulty annealing.

28. E. Berger

"The Theory of Glass Formation and Glassy State," Kolloid-Beihefte, 36, 1-42 (1932); Chem. Abs. 26, 4928 (1932).

The most important results of recent glass investigations are summarized in a theory of glass formation and glassy state which is correlated with physical, chemical and colloidal-chemical knowledge. Extensive bibliography.

29. W. E. S. Turner

"New Methods of Investigation of the Constitution of Glass," Atti. Congr. Internat. Vetro. e. ceram., (Milan) pp. 551-65, Glashutte, 63, 794 (1933); Chem. Abs. 29, 5231 (1935).

The methods which separate glass into definite chemical components and those which attempt to show the nature and properties of the glassy state are included. The first type is based on the equilibrium diagram, the second is concerned with the question of whether glass is a solid body or is an undercooled liquid. It is concluded that definite compounds exist in the glassy state.

30. J. T. Randall and H. P. Rooksby

"X-ray Diffraction and the Structure of Glass," J. Soc. Glass Tech., 17, 287-95 (1933).

The examination included some common glasses and Bi_2O_3, Sb_2O_3, $Cd_2P_2O_7$, $Li_2B_2O_4$, Se and $PbSiO_3$. The diffraction bands are explained on the basis of minute crystals or groups of atoms regularly arranged over small volumes. As suggested the probability of the formation of the glass is high for these substances whose normal crystal forms have forces binding the atoms together in either a strongly directional or in a localized matter.

31. B. Lengyel

"Structure of Glass," Magyar Chem. Folyoirat, 39, 73-82 (1933).

A summary of present theories on structure and molecular architecture of glass.

32. W. Weyl and E. Thumen

"Constitution and Color of Chromium Glasses," Sprechsaal, 66, 197-99 (1933); Chem. Abs. 28, 6261 (1934).

The green color of technical Cr glasses is due partly to the bluish green Cr^3 compounds and partly to yellow Cr^4 compounds. The effect of alkalies on the position of the oxidation equilibrium of Cr glasses is discussed. Addition of B_2O_3 deepens the color, which is probably due to the formation of complexes.

33. W. Weyl and E. Thumen

"Constitution of Glass, II. Theoretical Basis of Glass Coloring," Glastech. Ber., 11 (4) 113-20 (1933); Cer. Abs. 363 (1933).

It is shown by single examples how it is possible to obtain on the basis of exact absorption measurements in the visible region an insight into the nature of glass coloration. Thus the oxidation equilibria in Mn and Cr glasses can be quantitatively fixed and further the dissociation and association equilibria between Ni and Co silicates and silicic acid as solvent can be studied. A far reaching analogy exists between glasses and solutions.

34. W. Weyl

"Constitution of Glass," Angew. Chem. 46 (3) 68 (1933); Cer. Abs. 184 (1933).

Physical-chemical methods to solve the problem of the constitution of glasses have given information as to the physical structure but lead to nothing definite as to the chemical nature of the glass forming molecules. The determination of the absorption spectrum of glasses seems to have filled the gap, however. For colored glasses there is an explanation of the dependence of color on the composition, the temperature, and on other factors. In glasses colored with Cr_2O_3 this relation has been solved. If the glass consists largely of acid oxides then the chromium enters into combination in the form of chromic compounds. If the glass contains basic compounds (alkalis) there is a possibility of the formation of chromate. Normal technical glasses contain both oxidation states. By adding arsenic the Cr^{+3} state is obtained exclusively. It is more difficult to obtain pure chromate glasses; in order to produce them melting must be done at an oxygen pressure of 250 atmospheres. The effect of additions of boric acids on the color of chromium glasses was studied.

35. B. E. Warren

"Structure of Silica Glass," Z. Krist., 86, 349 (1933); Chem. Abs. 28, 2237 (1934).

Vitreous silica shows a broad diffraction ring which is attributed to the strongest line (111) of cristobalite crystals about 15A. in size. There are three objections: (a) the band is slightly displaced; (b) silica glass does not show the cristobalite volume change between 200 and 300°; (c) heat treatment does not increase the sharpness of the band, although crystallites should grow larger and the diffraction effects sharper. It is concluded that silica glass consists of a non-crystalline network of silica tetrahedra. Each Si is surrounded by 4 0 ions, and each 0 is shared between two tetrahedra. Each tetrahedron has 4 nearest neighbors at 3.1A. and 12 next nearest neighbors at 5.0A. Beyond this the distances are indefinite. The intensity of scattering from such an arrangement agrees satisfactorily with the experimental data.

36. F. W. Preston

"Glass is a Salt," Glass Ind., 14, 85 (1933); Chem. Abs., 27, 5496 (1933).

That glass need not be a salt is pointed out in an attempt to clarify our ideas concerning the nature of glass.

37. W. Weyl

"Constitution and Color of Glass," Sprechsaal, 67, 405-6 (1934); Cer. Abs. 14, 7 (1935).

Weyl reviews researches made at the Kaiser Wilhelm Institute of Silicate Research and deals with the effect of various factors on the properties of glass, its coloring, and theories of the glassy state.

38. W. Weyl

"Constitution of Colored Glasses," Ind. Ver., 1, 107-10 (1934); Cer. Abs. 14, 135 (1935).

In Cr glasses the equilibrium between Cr^3 and Cr^4 plays an important role, but the equilibrium between the basic and acidic constituents depends on the base glass.

39. E. Preston and W. E. S. Turner

"Methods of Determining the Constitution of Glasses," J. Am. Ceram. Soc., 17 (2) 26-33 (1934); Cer. Abs. 56 (1934).

40. W. Weyl and E. Thumen

"Constitution and Color of Uranium Glasses," Sprechsaal, 67, 95-97 (1934); Cer. Abs. 7 (1935).

The colors of aqueous solutions of UO_2 salts are compared with those obtained from similar compounds in glasses by means of light absorption studies. The effects of Na, K and B in the glass on its color are shown.

41. B. E. Warren

"The Diffraction of X-rays in Glass," Phys. Rev., 45, 657-61 (1934).

X-ray diffraction patterns of vitreous silica and germania were made with monochromatic radiation. The observed pattern can be calculated on the assumption that each Si is surrounded tetrahedrally by four oxygen atoms at a distance of 1.60A., the tetrahedra being then linked together irregularly. Vitreous GeO_2 has a similar structure with a distance of 1.65A.

42. B. E. Warren

"X-ray Determination of the Structure of Glass," J. Am. Cerm. Soc., 17, 249-54 (1934).

The method is useful for analyzing the x-ray diffraction patterns of amorphous solids. The atomic arrangements of two simple glasses have been worked out. In SiO_2, each Si is tetrahedrally surrounded by 4 0 at a distance of 1.6A. and each 0 is shared between two such tetrahedral groups. The mutual orientation of the 2 groups about their common direction of bonding is random, and hence it is a random 3-dimensional network. The configuration does not repeat at regular intervals, and hence is non-crystalline; this feature distinguishes the glassy state from the crystalline.

43. E. Preston and W. E. S. Turner

"Methods of Determining the Constitution of Glasses," J. Am. Ceram. Soc., 17, 26-33 (1934).

The equilibrium diagram method involves the destruction of the glassy condition but indicates the compounds that may be formed. The meaning of the change in state at about 40° below the softening point is still obscure. Light absorption studies indicate solvation. Data on specific volume, thermal expansion and index are not decisive. Electrical resistance data indicate the presence of $Na_2O{\cdot}2SiO_2$. Volatilization data indicate the presence of $Na_2O{\cdot}2SiO_2$ and $K_2O{\cdot}4SiO_2$.

44. K. R. Dixit

"Electron Diffraction in Glasses," Phys. Zs., 35, 141 (1934).

East electrons were reflected on opaque quartz, transparent quartz, pyrex, soda glass, heavy glass, cover glass and opal glass. The surfaces of the first six were plane and all gave a diffuse Deby-Scherrer ring corresponding to 1.5A. In the case of opaque quartz the intensity of the point was greatest. 1.55A is the Si-O distance. It was believed remarkable that polishing which usually destroys crystalline structure in this case causes the appearance of the interference point, when unpolished glasses show a completely random arrangement.

45. G. L. Clark

"X-ray is Answering the Question 'What is Glass'," Ceram. Ind., 24, 34, 36, 38 (1934).

46. George W. Morey

"Constitution of Glass," J. Am. Ceram. Soc., 17 (11) 315-28 (1934); Cer. Abs. 7 (1935).

47. B. E. Warren

"Atomic Arrangement in Vitreous Silica and Germania Dioxide," Phys. Rev., 45, 292 (1934); cf. Chem. Abs. 28, 2237 (1934).

48. W. Weyl

"Optical Investigation of the Constitution of Solutions and Glasses," Beiheft. Z. Ver. deut. Chem. Angew. Chem., 48, 573-75 (1935).

Structure of glass is discussed according to solvation processes.

49. G. Hagg

"Vitreous State," J. Chem. Phys., 3 (1) 42-49 (1935); Cer. Abs. 161 (1935).

The tendency of glass forming substances to supercool is discussed in connection with the existence of large or irregular groups and the melts of such substances. If the size of these groups makes their direct addition to the crystal lattice difficult and if the forces within them are strong enough to prevent a rapid disintegration of the groups, the melt will tend to supercooling and glass formation. In the inorganic glasses, consisting of oxides metalloids already corresponding acids or salts, the formation of large or irregular groups is caused by the strong tendency of these metalloids to coordinate oxygen in a definite way. If the number of the available oxygen atom is smaller than necessary for the formation of discrete polyhedral groups for the required coordination, the polyhedra will be linked together, sharing oxygen atoms. The resulting groups will delay crystallization and thus cause the formation of glass.

50. W. H. Zachariasen

"Vitreous State," J. Chem. Phys., 3 (3) 162-163 (1935); Cer. Abs. 161 (1935).

The general applicability of Zachariasen's theory for the structure of the vitreous of solids is given, and a comparison is made with Hagg's general theory.

51. N. A. Schishakov

"Constitution of Glass," Sorena, 52-56 (1935); Cer. Abs., 297 (1937).

52. W. Weyl

"The Constitution of Glasses as Determined from Optical Researches," Z. Elektrochem., 41, 472-6 (1935).

The properties of various glasses as determined from the nature of their absorption spectra are discussed. Colored ions are used as indicators.

53. B. E. Warren and A. D. Loring

"X-ray Diffraction Study of the Structure of Soda-Lime Glass," J. Am. Ceram. Soc., 18, 269-76 (1935).

Seven different compositions varying from 0 to 46% Na_2O were studied. For small soda contents the patterns show a single strong peak at Sin θ/λ = 0.12; with increasing soda this peak diminishes in intensity, while a new peak at Sin θ/λ = 0.18 gradually becomes more pronounced. There is no abrupt change in patterns. A random network picture of the glass is developed and upon this basis x-ray intensity curves can be calculated in good agreement with experimental curves. Each Si is tetrahedrally surrounded by four oxygens. Part of the oxygens are shared between two silicons, the others are bonded to only one silicon. The double bonded oxygens build up a continuous Si-O framework. The Na atoms are located at random in the various holes in this network. There is no evidence for the existence of compounds in the range of composition studied.

54. O. Knapp

"The Constitution of Silicate Glass," Keram. Rundschau, 43, 423-4 (1935).

Comparison was made of index calculated and measured. It was concluded that the composition of many glasses cannot be explained by the equilibrium diagram.

55. George J. Bair

"Constitution of Lead Oxide-Silica Glasses: I, Atomic Arrangement, II, Correlation of Physical Properties with Atomic Arrangement," J. Am. Ceram. Soc., 19 (12) 339-58 (1936); Cer. Abs. 11 (1937).

56. N. Valenkov and E. Porai-Koshitz

"X-ray Investigation of the Glassy State," Nature 137, 273-4 (1936).

Changes in the x-ray diffraction pattern on transition from vitreous silica to a crystalline mixture of cristobalite and tridymite are shown. Similar transition patterns were obtained by prolonged heating of sodium silicate glasses. This gradual change in pattern indicates the absence of a sharp boundary between the glassy and crystalline states.

57. W. Bussem and W. Weyl

"The Constitution of Glass," Naturwissenschaften 24, 324-31 (1936); C. A. 31, 229 (1937).

A review of previous work.

58. W. Schutz

"The Glass Pb_2GeO_4 and the Corresponding Crystalline Silicate, Pb_2SiO_4," Sprechsaal, 69, 270-71 (1936).

Compound's space characteristics are discussed.

(To be continued in September)

THINGS ARE HAPPENING IN GLASS COLORS

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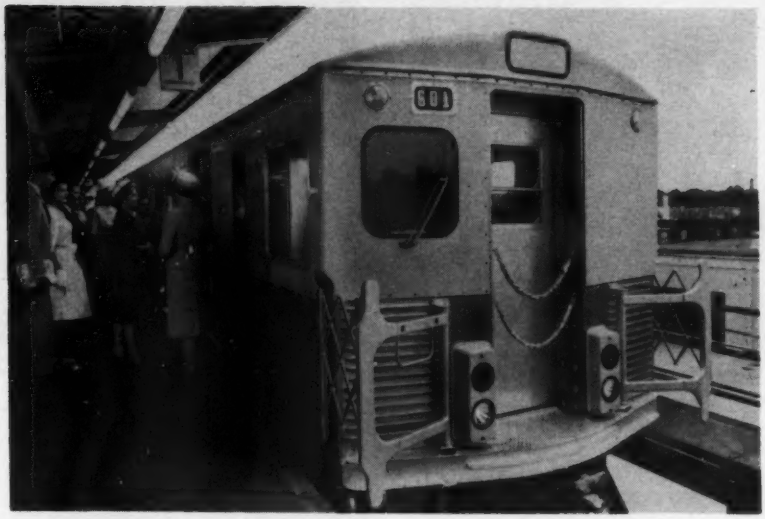


Fiber Glass in Subway Cars

● THE FIRST SUBWAY CAR EVER MADE of stainless steel and fiber glass was put into operation last month by the Philadelphia (Pa.) Transportation Company. Altogether, the city has ordered 270 cars from the Budd Company in Philadelphia, with complete delivery expected by January, 1961.

It is the use of stainless steel and fiber glass itself which is the most significant advancement in the new cars. Because of the lighter weights of these materials, it is possible to construct transit cars weighing on the average of 51,000 lbs. each. The lightest cars of their size ever built, they are about 6,000 lbs. less than the estimated weight of a conventional steel car based on the same specifications.

In terms of operating economy, this means a saving in electric power equal to $1.50 per pound over the 35-year depreciated life of the cars, or a total of $2,430,000.

In terms of maintenance—no periodic painting and no corrosion repairs will be needed—the city of Philadelphia estimates the saving at $28 per car per year, equalling $4,044,000 during the 35-year life span of the cars. Altogether this amounts to a saving of some $6,500,000.

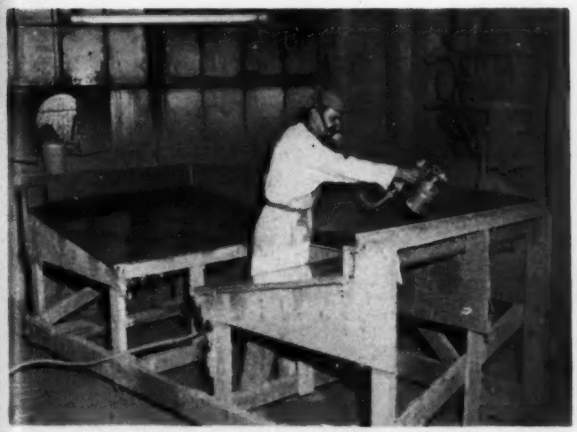


FIG. 1. Completed female fiber glass reinforced plastic mold is being sprayed prior to starting production cycle of front unit. This gel coat, although applied first, is finish coat of unit.

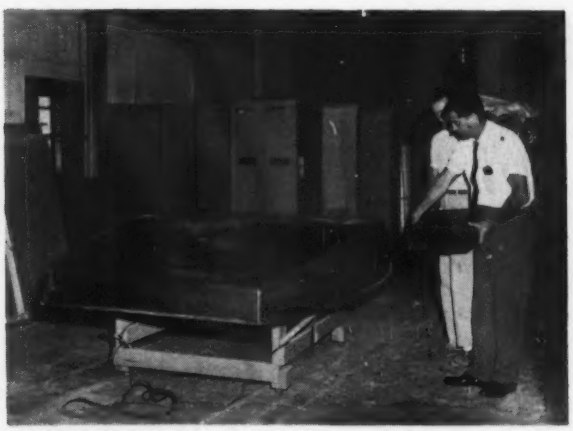


FIG. 2. Male wood pattern of front subway unit. A. R. Pollack, president, Modular Molding Corp., is holding insert which may be interchanged with one in pattern to produce rear subway unit.

FIG. 3. Several layers of fiber glass being cut to pattern at one time. Number of layers cut simultaneously varies with thickness, angle of cut, and slipperiness of fiber glass.

FIG. 4. Successive layers of fiber glass are applied to mold and are impregnated with flame retardant polyester resin. Extra strength is achieved in stress areas by adding more layers.

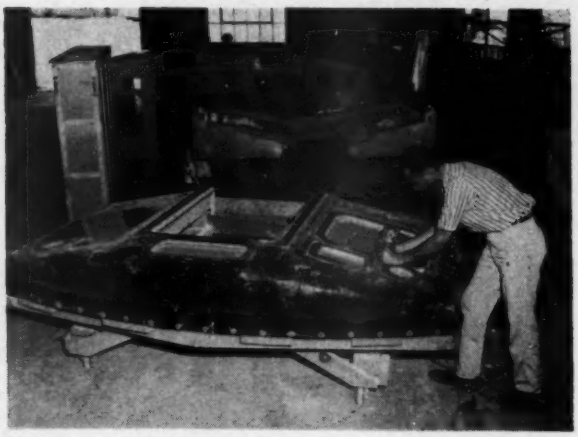


FIG. 5. Fiber glass shell is placed in drill and routing jig. Window cut outs are routed; required mounting holes are drilled and countersunk. Jig is made of fiber glass as well.

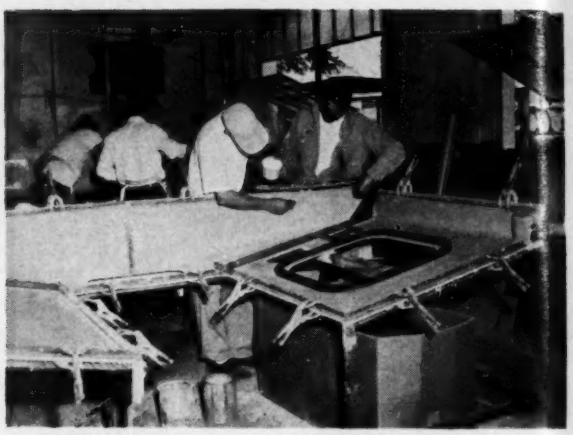


FIG. 6. Stainless steel inserts are molded into fiber glass shell (around window) and fiber glass strips are bonded to perimeter with epoxy resin. Note special arrangement of conventional clamps.

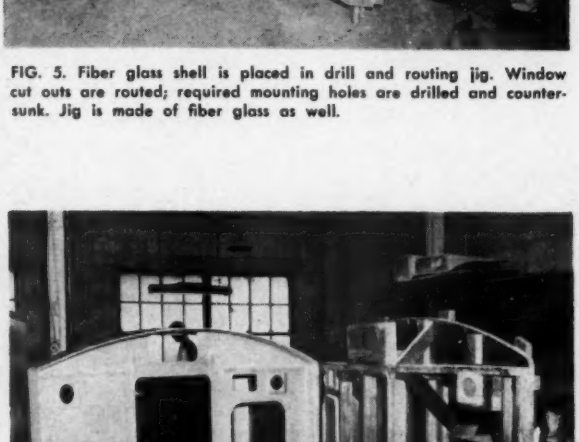


FIG. 7. Inside of finished fiber glass subway car front. At right is installation and inspection fixture which simulates mounting structure of car and is used for checking accuracy of unit.

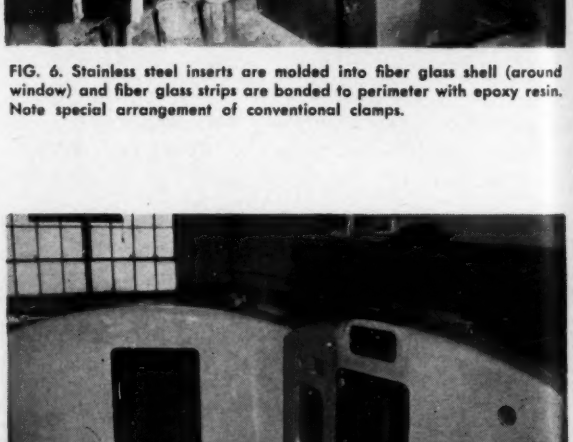


FIG. 8. Shell fixture (right) is for front and back of regular subway cars; other is for cars permanently coupled. Note door, motorman's window, destination window, car number and running light windows.

FIG. 9. and 10. Housing for subway car lights being removed from mold (left) and placed in a drill and routing fixture. Operator is routing mounting holes and window cut outs.

Molded fiber glass, which has the highest strength-to-weight ratio of all structural materials, is used in the fabrication of the front and rear sections of each subway car. Although fiber glass already has many applications* in the transportation field, this is the first time it has appeared in the subway car and marks an important milestone in the fiber glass industry.

By using molded fiber glass, Modular Molding Corp., Trenton, N. J., is producing these large end units without a high tooling cost, even though they have compound curvature details, and still maintaining the great strength and high corrosion resistance of stainless steel.

After considerable study by the engineers of Modular Molding and the Budd Company, final drawings and specifications were developed for the front unit, signal light housings, and motorman window trim. The tooling costs were reduced further by making one basic wood pattern (Fig. 2), designed with a removable section at the top which could be replaced with an insert. From this it was possible to make one female fiber glass reinforced plastic mold for each of the two types of car units by using the one pattern and interchanging the replaceable sections.

The fabrication of the subway car units begins by spraying the mold (Fig. 1) with the final finish as the first step. This finish, a gel coat, is a specially formulated flame retardant and abrasion-resistant polyester resin which has the stainless steel colored pigment dispersed in it so that it will blend with the stainless steel exterior of the car.

The fabrication process can best be understood by recognizing that the finished part is made from the outside in. Therefore, the final finish is applied to the mold first, then the laminations of fiber glass and resin. When the completed part is lifted off the mold, the final finish is no longer on the surface of the mold but has adhered to the fiber glass unit as a stainless steel-colored coat.

After the gel coat, or overlay, has set up, successive layers of fiber glass mat[2], which have been previously

(*Continued on page* 462)

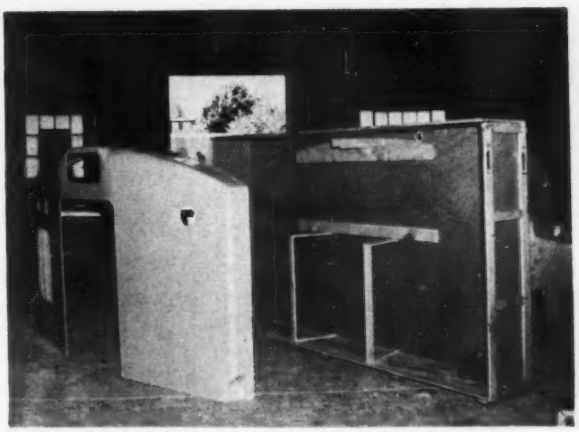


FIG. 11. After the fiber glass car front is completed and inspected, it is packed in a special shipping crate. Note fitting and mounting details in crate.

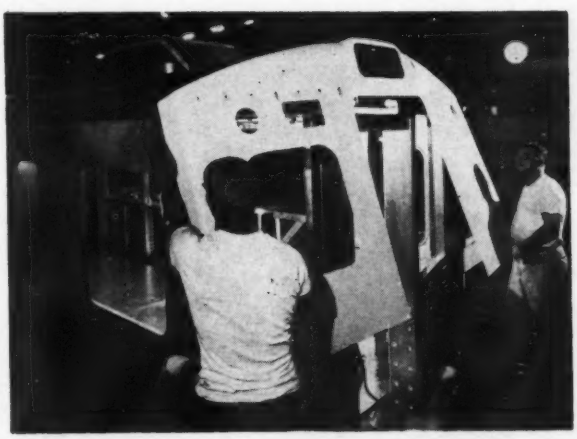


FIG. 12. Installing fiber glass front on subway car at the Budd Company assembly line. Surface is color impregnated with a light grey to match stainless steel exterior of cars.

* See "Major Applications in Fiber Glass", THE GLASS INDUSTRY, June, 1960, p. 341.

• FIBER GLASS •

EQUIPMENT & SUPPLIES

CHOPPED STRAND. High strand-integrity, chopped fiber glass for reinforcing pre-mix type molding compounds. Said to facilitate a more homogeneous molding material which results in greater uniformity of finished parts and eliminates surface distortion and non-uniform strengths througout the molded part. Available in ¼" lengths.

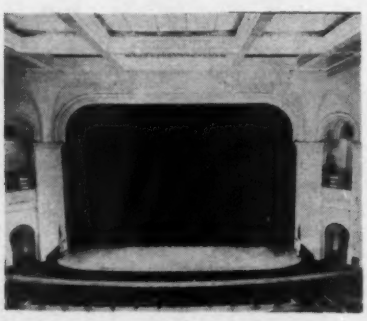
PROTECTIVE SPRAY COATING of fiber glass flake provides a corrosion-resistant surface to metals, wood and concrete. Vapor transmission: less than .01 perms. Shear strength: 800 psi. Dielectric strength: 500 volts per mil. Can be utilized where corrosion is a major problem or as a water sealant for concrete block and slab walls. A 20-mil thick coating contains 50 layers of fiber glass flake. Spray gun unit especially designed for the product is also available.

Chopped Strand: J. S. McBride, Owens-Corning Fiberglas Corp., 717 Fifth Ave., New York 22, N.Y.
Spray gun unit: De Vilbiss Co., 300 Phillips Ave., Toledo 1, Ohio.

APPLICATIONS

FIBER GLASS CURTAIN was recently installed in the auditorium of the American Museum of Natural History, New York City. This curtain consists of 400 yards of vinyl-coated fiber glass fabric. The curtain is flame-resistant, dimensionally stable, rot-proof, requires no dry cleaning and is unaffected by deteriorating effects of sunlight and moisture.

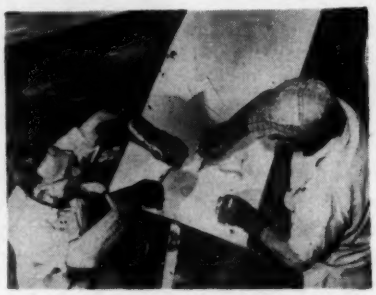
Coated Glass Fabric: Duracote Corp., Ravenna, O.
Fiber Glass: Owens-Corning Fiberglas.



SILICONE RESIN. Solventless silicone resin for high-temperature insulation is used in the manufacture of fiber glass reinforced spacer bars for transformers. Now commercially available to the electrical and electronic industry for use in form-wound coil impregnation, lamination using wet lay-up techniques, and potting and encapsulation. Can be combined with organic monomers to provide tailor-made insulating resins. Eliminates the need for solvent removal during curing. Furnished in pint, gallon, 5-gallon and 55-gallon containers.

Silicones Division, Union Carbide Corp., 270 Park Ave., New York 17, N.Y.

FIBER GLASS COVERING is being used on the hulls of the "glass-bottom" boats at Florida's famous Silver Springs. The electric-powered crafts, 27 in all, have been in use since 1924 and every five years each boat has required extensive repairs in addition to repeated paintings. Now the boats are out of the water for only a week or 10 days and return to duty with a much longer in-water expectancy. Painting will consist of "fresh-up" coats above the water line. In applying the fiber glass roving the boat must first be completely dried out ashore. Then is it carefully sanded around the plate glass compartment to remove the grime. Epoxy surfacing compound is brushed on the wood and the roving is applied. Later the compound is squeezed into and through the fiber glass, bonding the two into one durable surface. For extra protection and smoothness an additional coat of epoxy compound is applied and troweled down.



Fiber Glass: Johns-Manville Fiber Glass Corp., Toledo, O.
Supplier: Glass Plastic Corp., Linden, N.J.

FIBER GLASS JET SPRAY ROOFING METHOD uses a spray gun to apply asphalt or other materials and glass fibers simultaneously, resulting in a single monolithic film. Method can be applied upon either commercial and industrial roofing or on non-conventional roofs of free form design. A 3-man crew using the gun can install between 15,000 to 18,000 sq. ft. of material a day. Under conventional methods a 5-man crew installs approximately 8,000 sq. ft. of material a day. The seamless coating can be applied in sidewalls or insulation, maintenance and repair, sound deadening and pipe coating; and as a corrosive protection in water tanks.

The gun employs twin ejectors for clay-stabilized asphalt compound that work in conjunction with a separate ejector for special glass roving. Roving is treated and flows into a glass-cutter in the gun as a ribbon. There are 50,000 glass filaments per sq. in. of ribbon. A 100 sq. ft. of roofing area requires about 8-10 gallons of coating and approximately 100 lbs. of glass fiber roving. A single trigger controls all three ejectors and the coating material is forced through the hoses and twin ejectors by a pump and compressor. Applied by franchised applicators, the Monoform System roofs are eligible for 20, 15 or 10-year surety bonds.

Spray Gun: SealZit Company of America, 3640 Chicago Ave., Riverside, Calif.
Roofing Method: The Flintkote Co., 30 Rockefeller Plaza, New York 20, N.Y.

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FOR OVER 60 YEARS THE GLASS INDUSTRY'S PARTNER IN PROGRESS

NEWS
IN THE GLASS INDUSTRY

Personalities...

William J. Stewart

R. C. Conover

William J. Stewart

Elected president and general manager of Kimble Glass Company, subsidiary of Owens-Illinois. He began with Owens-Illinois in 1930 as an accountant at the Charleston, W. Va., plant. Before becoming chief industrial engineer, Glass Container Division, in 1945, he served company plants in Huntington, W. Va., Alton, Ill., Terre Haute, Ind., and Gas City, Ind.

Raymond H. Mulford, president of Kimble since 1956, is transferring to the O-I Administrative Division. W. Boyd Owen, succeeds Stewart as director of personnel administration, and has also been named a vice president of the Administrative Division.

W. E. Benke

Elected to the board of directors of H. I. Thompson Fiber Glass Company, Los Angeles. Benke has been with the company since 1944 and is currently serving as vice president of sales. Robert L. Potter has joined the sales department.

Pittsburgh Plate Glass Co.

Was honored for its outstanding support and advancement of the training profession by the American Society of Training Directors at their 16th Annual Conference in St. Louis.

Robinson F. Barker, vice president and general manager, glass division, Pittsburgh Plate, was presented with a plaque by Robert A. Graham, executive vice president of the Society. It is the first time the group has presented this type of award to an industrial firm.

ASTD consists of approximately 4,000 members from U.S. industrial and commercial firms, and government agencies, and has 70 chapters in this country and overseas.

R. C. Conover

Named general works manager, Refractories Division, H. K. Porter Company, Inc. He will supervise operations of the Division's 15 refractories plants located throughout Alabama, Ohio, Colorado, Pennsylvania, Missouri, Illinois, Connecticut and Mississippi. He was previously Western district works manager.

Emil Ott

Resigned as vice president, Research and Development, Chemical Divisions, for Food Machinery and Chemical Corporation. He will continue as part-time consultant for the company and will also devote his time to academic activities. Dr. Ott served as research director for Hercules Powder Company for 16 years and prior to that position he was on the chemistry faculty of John Hopkins University.

Norman J. Vang

Named assistant to the staff vice president of Corning Glass Works. He is succeeded by LeRoy A. Amylon as director of industrial relations. Allen W. Dawson is manager of the television bulb sales department in the Electrical Products Division, and Malcom H. Hunt succeeds Dawson as manager of the electronic components department. S. Joseph Muccigrosso is manager of product development for the Electrical Products Division.

Pittsburgh Plate Glass Co.'s Robert B. Burr, (left), manager of training and development, and Robinson F. Barker, vice president and general manager of the Glass Division, admire plaque presented to the Company by American Society of Training Directors at their 16th annual conference. Plaque honors Pittsburgh organization for its outstanding support and advancement of the training program.

Soon To Be Published Vol. II. HANDBOOK OF GLASS MANUFACTURE

Volume I of the Handbook of Glass Manufacture was originally published in 1953 by the Ogden Publishing Company. Uninterrupted demand for the book necessitated a second printing in 1957 in order to meet the needs of all those concerned with glass manufacture, technology and engineering. Both the first and second printing of Volume I have been sold out.

As a supplement to the first edition, Volume II of the Handbook of Glass Manufacture will be published on August 15, 1960, and will again be edited by Dr. Fay V. Tooley, Professor of Glass Technology, Department of Ceramic Engineering, University of Illinois.

CONTENTS . . .

Chemical and Instrumental Analysis of Glass
Francis Glaze, Consultant
John Time, Owens-Corning Fiberglas Corp.

Optical Properties of Glass: Effects of Radiation on Glass
Norbert J. Kreidl, Bausch and Lomb Optical Co.

Scientific Glass Blowing
Vincent DeMaria, Glass Products Development Laboratory

Flat Glass Manufacturing Processes
Roy G. Ehman, Pennsylvania State University

The Quality Control Chart
Ronald Wiley, Owens-Corning Fiberglas Corp.

Electric Melting of Glass
Larry Penberthy, Penberthy Electromelt Co.

Constitution and Structure of Glass
Fay V. Tooley, University of Illinois

The Glass Industry
55 West 42nd Street, New York 36, New York

Date.....

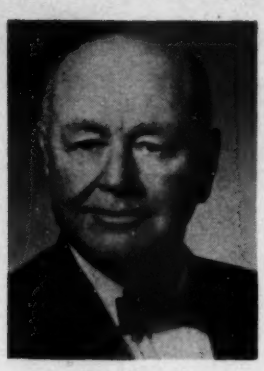
Enclosed please find remittance in the amount of $..... to cover the cost of ..... copy(ies) of Volume II of the HANDBOOK OF GLASS MANUFACTURE. Single copy price, $10.00. Order for 5 or more copies, 10% discount. Add Shipping and Insurance charges, domestic 60¢ per copy; foreign 90¢ per copy. Foreign remittance in U.S. dollars.

NAME.....

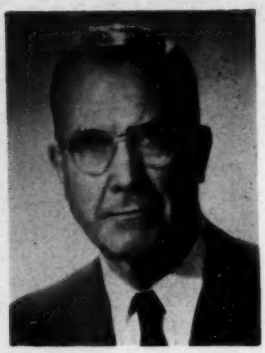
COMPANY.....

STREET..... CITY..... STATE.....

Don L. Hinmon



H. L. Monteith



H. S. Steece

Don L. Hinmon

Appointed to the newly-created office of senior operating vice president for Johns-Manville. He will administer three of the company's corporation operating divisions, one of which is the Fiber Glass Division, Toledo, O.

Charles E. Nicolas

Named special assistant to John H. Goodwillie, plant manager, of Libbey-Owens-Ford Glass Company's Shreveport, La., window glass plant. Nicolas will have primary responsibility for the extensive furnace rebuilding program to be carried out under Mr. Goodwillie's direction.

H. L. Monteith

Former regional sales promotion manager, and H. S. Steece, former district manager of distributor sales, retired from the field of sales organization of Libbey-Owens-Ford Glass Company after serving 26 years and 17 years, respectively.

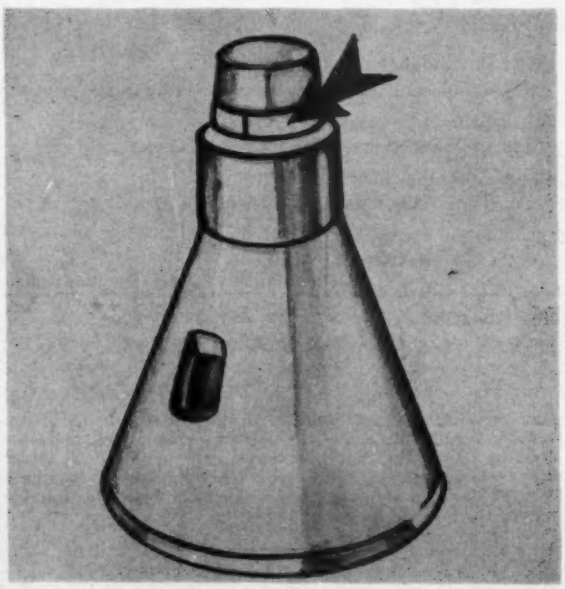
J. A. Hughes

And W. H. McConnell have been elected senior vice presidents, Diamond Alkali Company. J. W. Mantz is director of trade development; A. B. Tillman was named general manager, Soda Products, Chrome Division and F. W. Jarvis, general manager, Electro Chemicals Division.

Companies...

Project Mercury Capsules

Are being equipped with thin, cylindrical shields of glass through which radio signals will flash the condition and position of the first American in space (see cover). Corning Glass Works is producing the shields and also special glass for the capsule viewports.



Arrow locates glass antenna shields on Project Mercury capsule. Corning Glass Works manufactures the shields and also produces special glasses for capsule viewports. Viewport is shown in lower part of drawing.

Each of the 12 capsules will use three curved, translucent sections of the company's 96 per cent silica glass to protect the transmitting and receiving antennas during re-entry heat and shock. The glass is only $\frac{1}{8}$-inch thick, just over $6\frac{1}{2}$ inches in height, and curves through approximately two feet in each section. It will withstand continuous operating temperature of 900°C, and intermittent temperatures up to 1200°C.

Critical information will flow through the glass to earth about the astronaut's heart rate, blood pressure and body temperature, the capsule's acceleration, possible landing points and such functions as oxygen pressurization. The glass shields also permit voice communications to be transmitted and received.

Libbey-Owens-Ford Glass Co.

Reducing operations and employment at its Ottawa, Ill., plants. Among the factors responsible for the decision to reduce the glassmaking operations is (1) the substitution of tempered solid safety glass by most American car manufacturers for laminated safety glass in side windows, (2) foreign car imports, and (3) reduced glass requirements resulting from compact models becoming a larger percentage of American built cars.

Owens-Illinois

Awarded a contract for the construction of a multi-furnace, 150,000 sq. ft., glass container plant in New Orleans to Keller Construction Corporation. Plant site is a 24-acre plot on the Inner Harbor Industrial Canal leased for 99 years from the board of commissioners of the Port of New Orleans. It will be the company's 17th plant for the manufacture of bottles and jars and is expected to be in operation by mid-1961.

The company's glass container plant near Bogota, Colombia, has begun production and will be manufacturing between 50 and 75 million containers annually by the end of next year. It will supply bottles and jars for food, drugs, beverages and chemicals for the Colombian market.

Quartz Sand Deposit

Suitable for glass manufacturing has been discovered near Kapiri Mposhi in Northern Rhodesia. Located by the Geological Survey Department it is the only known deposit of quartz sand in the territory and probably the only deposit in the Central African Federation.

Direct inquiries from several glass manufacturing companies resulted in the investigation which located approximately 100,000 tons of sand. The deposits in the Kapiri Mposhi Hill area can be used in the manufacture of containers, window panes and similar products however, it does not seem suitable for high-quality glass such as optical products.

Among the glass manufacturer inquirers was Pilkington Bros., Ltd., who is constructing a £300,000 glass plant at Umtali. It is intended to meet the demand from the rapidly expanding motor trade in the Federation and is expected to be in production in a year. The Pilkington Company will work in conjunction with Plate Glass and Shatter-Prufe Industries, Ltd., manufacturers of laminated safety glass at Port Elizabeth.

Johns-Manville Corp.

Placed into operation what is said to be the most extensive industrial teletype network on the North American continent. The system is expected to save the company around $200,000 a year in communications costs. Capable of transmitting 340,000 words per day, it connects the Waterville, O., plant with five other plants of the Fiber Glass Division, and 63 other plant, mine, and sales locations spreading from North Bay, Ontario, to New Orleans, and from New York and Boston to San Francisco. The network also furnishes inter-communication between each station on the line.

The nine-circuit, 11,000 mile line drastically reduces the number of relays once necessary under the former system, and expedites wire traffic estimated to exceed 90,000 messages. At one time, a message originating from Toledo, O., had to be sent to Chicago and then be relayed to Waterville, O., a nearby town only 11 miles away.

Cambridge Wire Cloth

Opened a new sales territory extending from upstate New York through Massachusetts, Rhode Island, Maine, New Hampshire and Vermont. James A Shuttleworth has been appointed to handle the newly opened district and the headquarters will be at 279 Broadway, Stoneham 80, Mass.

Clark-Schwebel Fiber Glass Corp.

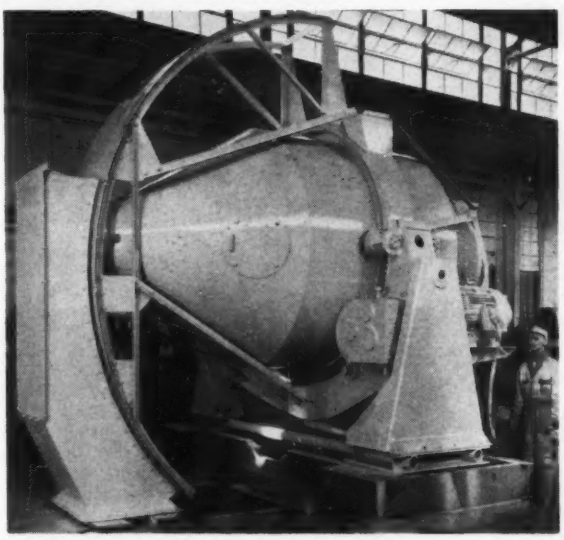
A new entry posted by M. Lowenstein & Sons, Inc., in the glass fabric field. The company will run as an independent affiliate of the firm and will be headed by Raymond F. Clark, president, and Jack P. Schwebel, executive vice president. The firm will weave, finish and market industrial and decorative glass fabrics. Mr. Schwebel founded his own glass weaving firm in 1952 which he later sold to J. P. Stevens & Company, Inc.

American Scientific Glassblowers Soc.

Was told at its Fifth Annual Symposium in Pittsburgh that its profession, once jealously guarded, has become an important link connecting all the fields of science.

The message was given by Dr. Blaine B. Wescott, executive vice president and director of research, Gulf Research & Development Company, Harmarville, Pa. He also indicated that the Harmarville operation made extensive use of glass-blowing techniques to speed oil exploration and production.

The symposium included the paper, "Gas Adsorption on Solid Surfaces," by Dr. Donald S. MacIver, Physical Science Division, Gulf Research; and a talk concerning the handling of radioactive glass by Henry L. Christie, The Atomic Energy Commission of Canada, Ltd., Ottawa.



Capable of producing 126 cu. ft. batches on as low as a three-minute cycle, this giant glass batch mixer has been completed for installation by T. L. Smith Co., Milwaukee, for a large Eastern glass plant. A tilting discharge type, the 35,000 lb. machine remains completely dust-sealed throughout the entire cycle of charging, batching, and discharging. The manufacturer expects the unit to provide the glass industry with new standards of efficient production in high-volume batching operations.

Tyre Bros. Glass Co.

Nearly tripled receiving and storage efficiency in their southern California plant. The large mirror manufacturer and glass wholesaler using the services of W. B. Semco & Associates, Los Angeles industrial consultants, installed a bridge crane that handles glass cases quickly to and from any point in the receiving and storage area. To increase the storage space "high stacking" was used. Stiffeners consisting of 3 x 1 channels were welded to columns along the walls and lock braces were devised for easy attachment and removal from the stiffeners. The braces hold the big wooden cases steady even when the stacking reaches 20 feet in height. The crane has a 2-ton capacity electric hoist driven by a 2-speed motor.

Weber Glass Machinery Division

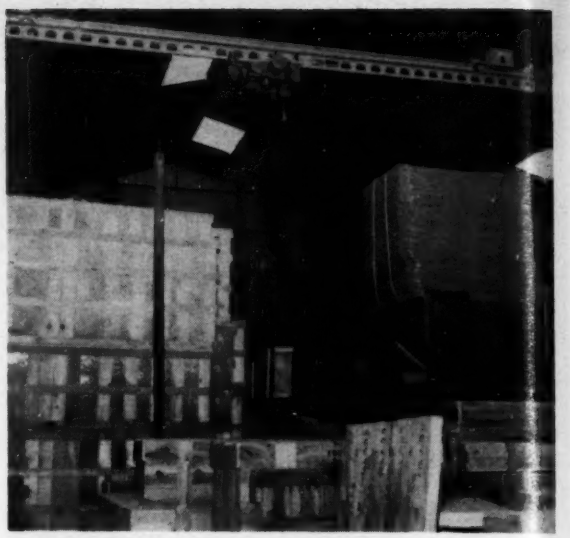
Sold and transferred, as of July 1, to Weber Aircraft Corporation, a wholly-owned subsidiary of Weber Showcase & Fixture Company Inc. Fred A. Good is manager of the new division.

The glass machinery division was responsible for the development of an automatic straight glass edger; straight and circular glass beveling machines and straight marble edge grinding and beveling machines.

Pittsburgh Plate Glass Co.

And the United Glass and Ceramic Workers of North America extended their labor contract covering approximately 10,000 glass workers, until February 16, 1962.

Lightweight telescope disks of sandwich-type construction developed by Corning Glass Works for use in missiles, satellites and aircraft. Mirrors consist of two plates of fused silica, held apart by the same material in forms of ribs or tubes. This type of construction is for the weight-saving achievement vitally needed in compact telescopes for outer space photography.



High stacking is solution for increased storage area at Tyre Bros. Glass Co. Crates at left are stacked 20 ft. high by overhead crane. Special lock braces attached to stiffeners along wall stabilize the glass crates.

Shatterproof de Mexico

(Subsidiary of Shatterproof Glass Corp., Detroit) has completed their relocation into larger quarters, in order to meet increased demands for laminated safety glass in Mexico. The new 24,000 sq. ft. plant is capable of producing 100,000 sq. ft. of laminated safety glass per month.

Libbey-Owens-Ford Glass Co.

Is marketing a new selection of 26 patterns in decorative, rolled and wire glass through its distributors and dealers. The glass is manufactured by Pilkington Brothers, Ltd., Great Britain; LOF will be exclusive sales agent in the U.S. Ralph A. Prickett, formerly distributor sales manager for LOF at Los Angeles, Calif., has been appointed sales manager for patterned glass.

Corning Glass Works

Is producing new, lightweight, distortion-free mirrors of fused silica for missile, satellite, and airborne telescope systems.

Employing an unusual sandwich construction consisting of two silica plates separated by walls, ribs, or tubes of the same material which is fused to the plates by intense heat, the company reduces the size and weight of mounting and auxiliary equipment for the reflectors. The mirror weight itself can be reduced to half that of a solid disk with equal surface area, depending on design. Weight, of course, is a prime factor in aerospace telescopes, and a vital consideration of all space exploration. Since fused silica has a near-zero thermal expansion the mirrors will retain their shape and distortion-free images under sudden and extreme changes of temperature. Impurities in the material average less than one part per million and the blanks can be precision ground and finished with standard optical equipment.

EXPERIENCE IS THE ADDED PLUS AT HOMMEL

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Your Purchasing dollar buys more at The O. Hommel Company. It buys glass industry supplies backed by experience gained since 1891. Experience that pioneered the conventional and hot squeegee processes. Experience that annually broadens glass industry horizons with new and more resistant colors. Experience that maintains the highest quality control standards to assure uniform production.

GET FULL VALUE FOR YOUR PURCHASING DOLLAR

COLORS—Transparent and Opaque Enamels, Fluxes, Liquid Luster Colors, Ices, Burnish Gold and Silver, Paste Gold, Stamping Gold, Liquid Gold.

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ACID RESISTANT COLORS—Tableware and Laboratory Ware.

SULFIDE RESISTING COLORS — Tableware, Illuminating Ware and Cosmetic Jars.

SQUEEGEE PASTE for Hot and Regular Process.

CHEMICALS, MATERIALS AND OXIDES

Acids
Ammonium Bifluoride
Arsenic
Barium Carbonate
Bone Ash
Borax
Boric Acid
Cadmium Sulphide
Clays
Cryolite (Natural)
Feldspar
Fluorspar
Iron Chromate
Potassium Bichromate
Potassium Carbonate
Salt Cake
Selenium
Soda Ash
Sodium Antimonate
Sodium Bichromate
Sodium Nitrate
Sodium Silico Fluoride
Sodium Uranates
Sulphur
Zirconium Silicate

OXIDES

Chrome Green Oxide
Cobalt Oxide
Copper Oxide
Iron Oxides
Manganese Dioxide
Nickel Oxide
Tin Oxide
Titanium Dioxide
Uranium Oxide
Zinc Oxide
Zirconium Oxide

THE O. HOMMEL CO.

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West Coast — 4747 E. 49th Street, Los Angeles, California

HOMMEL

INVENTIONS AND INVENTORS

Sheet and Plate Glass

Laminated glass. Patent No. 2,831,792. Filed December 21, 1954. Issued April 22, 1958. No sheets of drawings; none reproduced. Assigned to Libbey-Owens-Ford Glass Company by Romey A. Gaiser.

The type of laminated glass structure with which this invention is particularly concerned comprises two sheets of glass and an interposed layer of non-brittle plastic adherent thereto to provide a composite structure and in which a surface of at least one of the glass sheets is provided with a transparent electrically conductive film.

The transparent electrically conducting film may be formed of tin oxide which may be applied in a number of different ways, per method described in Patent No. 2,429,420, granted October 21, 1947, to H. A. McMaster.

In fabricating the laminated glass structure, the laminations may first be cut to the desired size and then assembled in sandwich form. Any suitable jig means or the like can be employed to position the plastic layer between the glass sheets with the filmed or coated surface of the glass sheet preferably facing inwardly and lying adjacent the interlayer. As assembled, there is present between the laminations undesirable air, moisture, and/or gas which must be removed in order that an efficient bond be obtained between the respective laminae.

To accomplish this bonding effect, the superimposed sheets and plastic interlayer are placed in a suitable plastic bag. The plastic bag is formed of two sheets or layers of an air impervious plastic material and which are sealed together around their marginal edge. If desired, three sides of the sheet may be sealed before the components of the laminated structure are inserted therein, and after the glass has been placed in the bag thus formed, the fourth side may be sealed by a heating element or other suitable sealing means to complete the air tight sealing of the bag. The seal is formed around the leads or extensions which are suitably connected to the electrodes or bus bars thus allowing them to extend outwardly of the bag.

By extracting the air within the bag, the laminae are subjected to a pressure by the atmosphere on the outside of the bag which further forces the air from between the laminae and also assures uniform even contact between the plastic interlayer and the sheets.

There were 10 claims and the following references cited.

United States Patents

2,372,929, Blessing, April 3, 1945 and 2,552,955, Gaiser et al., May 15, 1951.

Tube and Cane Machines

Transfer tube mechanism. Patent No. 2,878,620. Filed January 29, 1958. Issued March 24, 1959. No sheets of drawings; none reproduced. Assigned to Sylvania Electric Products Inc., by James M. Calehuff and William L. Reiter.

The tube-cutting and glazing machine includes a tube-cutting unit having an intermittently indexed cutting turret and tube-cutting and feeding mechanisms for feeding a prescribed length of tubing in position for cut off transfer and a tube-glazing unit having an intermittently indexed glazing turret and rotatable glazing spindles on the glazing turret arranged to internally engage and support the cut lengths of tube, and is provided with a transfer unit which is interposed between the tube-cutting and tube-glazing units. The transfer unit is arranged to receive successive lengths of tube or tubing after cut off by the tube-feeding and cutting mechanisms and to deliver the cut lengths into supporting relation on the rotatable glazing spindles of the glazing turret, whereupon the cut lengths of tubes are revolved at a relatively high speed to attain centrifugal glazing at both ends of the cut lengths.

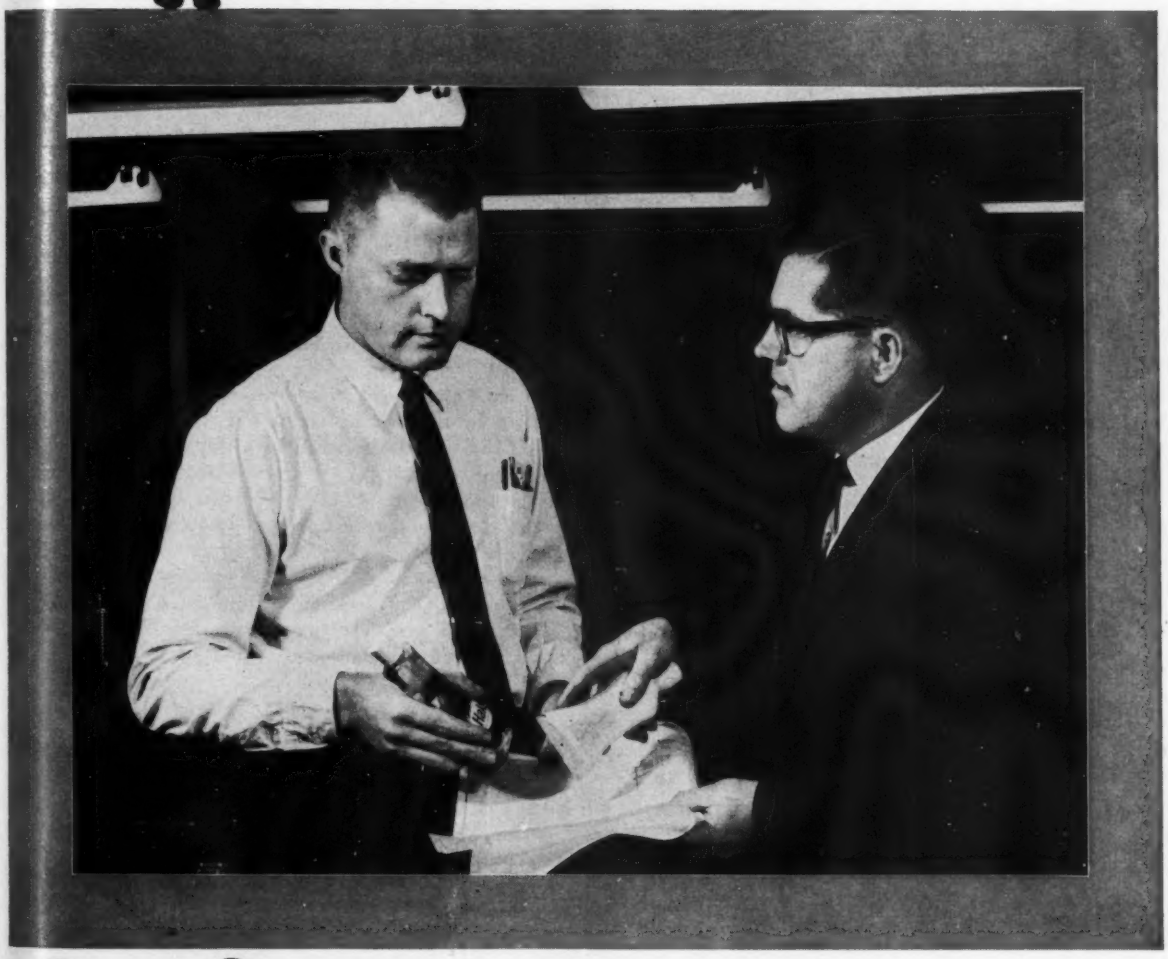
The transfer unit includes an intermittently indexed transfer turret and tube-receiving members, usually in the form of open ended tubular guides or sleeves. Closures are arranged to at least partially block the open lower ends of the tube-receiving members and to provide individual footings for the respective cut lengths of tubings during transfer from the cutting turret to the glazing turret. Suitable means are coordinated to the indexing of the turrets by the turret drive for moving the respective closures out of blocking relation to the tube-receiving members to enable the tube-receiving members to be cleared, preferably by the action of gravity, of glass fragments and particles. The timing of the movement of the closures out of blocking relation to the respective tube-receiving members is preferably such that during each transfer cycle successive tube-receiving members are open at their lower ends to clear the same of any particles which have accumulated therein during the operative portion of the transfer cycle.

There were 13 claims and the following references cited in this patent.

United States Patents

1,046,723, Beadle, Dec. 10, 1912; 1,546,353, Rippl et al., July 14, 1925; 2,004,492, McNamara et al., June 11, 1935; and 2,447,568, Eisler, Aug. 24, 1948.

Wash them right out of your hair... and, that's very often what can be done with glass production problems when engineering know-how is enlisted at the very beginning. That's why Paul Smith, Overmyer Chief Engineer, is so often called in at the inception of a new glass container. Consulting with either the designer or customer's engineers, he helps to make important money-saving decisions while, or even before, the project is still on paper. Can it be made? And is it practical? And often Smith is called upon to help achieve better, faster production from mould designs already in production. This willingness on the part of Overmyer executives and staff members to go beyond the call of responsibility is one of the reasons Overmyer has long had a part in the progress of glass.



OMCO **OVERMYER MOULD COMPANY, INC.**

General Offices: Winchester, Indiana • Factories in Winchester, Indiana
Fremont, Indiana • Greensburg, Pennsylvania • South Gate, California

CURRENT STATISTICAL POSITION OF GLASS

Employment in the glass industry during April, 1960, was as follows: *Flat Glass*: a preliminary figure of 27,400 for April, 1960, indicates a decrease of 9.2 per cent under the adjusted figure of 30,200 reported for March, 1960. *Glass and Glassware, Pressed and Blown*: an increase of 0.5 per cent is shown by the preliminary figure of 89,400 reported for April, 1960, when compared with the adjusted figure of 88,900 reported for March, 1960. *Glass Products Made of Purchased Glass*: the preliminary figure of 13,700 given for April, 1960 is 2.8 per cent under the adjusted figure of 14,100 reported for March, 1960.

Payrolls in the glass industry during April, 1960 were as follows: *Flat Glass*: a decrease of 9.5 per cent is shown in the preliminary $14,769,290.48 given for April, 1960, when compared with March's $16,323,052.28. *Glass and Glassware, Pressed and Blown*: a decrease of 2.7 per cent is shown in the preliminary $34,656,711.89 given for April, 1960, when compared with the previous month's adjusted $35,392,515.96. *Glass Products Made of Purchased Glass*: a preliminary figure of $4,252,107.22 was reported for April, 1960. This is a decrease of 1.2 per cent when compared with the adjusted figure of $4,307,218.65 for March, 1960.

Glass Container Production based on figures released by the Bureau of the Census, Industry Division, was 13,514,000 gross during May, 1960. This is an increase of 6.4 per cent over the previous month's production figure, 12,693,000 gross. During May, 1959, glass container production was 13,405,000 gross, or 0.8 per cent under the May, 1960 figure. At the end of the first five months of 1960, glass container manufacturers have produced a preliminary total of 65,801,000 gross. This is 5.3 per cent more than the 62,449,000 gross produced during the same period in 1959.

Glass Container Shipments during May, 1960 came to 14,151,000 gross, an increase of 10.7 per cent over April, 1960, which totaled 12,783,000 gross. Shipments during May, 1959 amounted to 13,541,000 gross, or 4.3 per cent less than May, 1960. At the end of the first five months of 1960, shipments have reached a preliminary total of 62,688,000 gross, which is 3.8 per cent more than the 60,359,000 gross shipped during the same period of the previous year.

Stocks on hand at the end of May, 1960 came to 20,358,000 gross. This is 3.0 per cent less than the 20,986,000 gross on hand at the end of April, 1960, and 8.7 per cent more than the 18,720,000 gross on hand at the end of May, 1959.

GLASS CONTAINER SHIPMENTS

(All Figures in Gross)

Narrow Neck Containers

	May, 1960
Food	1,343,000
Medicinal and Health Supplies	1,268,000
Chemical, Household and Industrial	1,016,000
Toiletries and Cosmetics	958,000
Beverage, Returnable	1,316,000
Beverage, Non-returnable	201,000
Beer, Returnable	796,000
Beer, Non-returnable	1,258,000
Liquor	801,000
Wine	417,000
Sub-total (Narrow)	9,374,000

Wide Mouth Containers

Food	*3,591,000
Medicinal and Health Supplies	398,000
Chemical, Household and Industrial	183,000
Toiletries and Cosmetics	281,000
Dairy Products	132,000
Sub-total (Wide)	*4,585,000
Total Domestic	13,959,000
Export Shipments	192,000
TOTAL SHIPMENTS	*23,321,000

*This figure includes Fruit Jars, Jelly Glasses, and Packers' Tumblers.

GLASS CONTAINER PRODUCTION AND INVENTORY

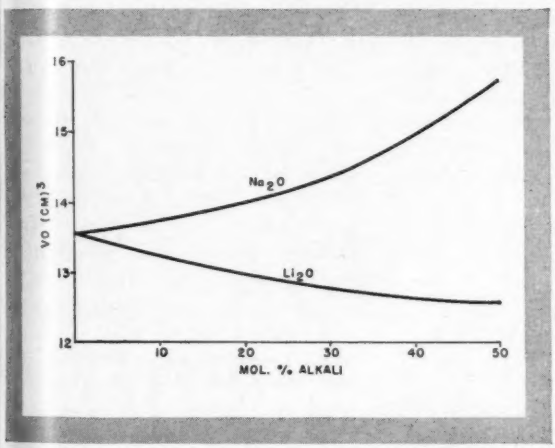
(All Figures in Gross)

		Production May 1960	Stocks May 1960
Food, Medicinal and Health Supplies; Chemical, Household and Industrial; Toiletries and Cosmetics	Narrow Neck	4,459,000	7,091,000
	Wide Mouth	*4,407,000	*6,696,000
Beverage, Returnable		1,312,000	2,529,000
Beverage, Non-returnable		246,000	319,000
Beer, Returnable		657,000	371,000
Beer, Non-returnable		1,122,000	847,000
Liquor		793,000	1,434,000
Wine		414,000	707,000
Dairy Products		104,000	364,000
TOTAL		*13,514,000	*20,358,000

*This figure includes Fruit Jars, Jelly Glasses, and Packers' Tumblers.

Tightening Glass Networks with the Lithium Ion

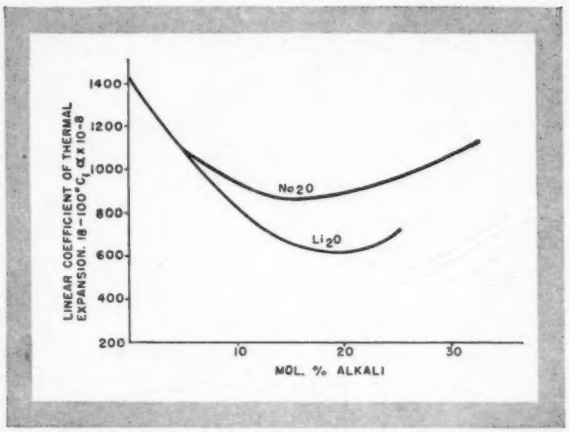
As an alkali is added to silicate glass, density measurements show a steady increase in the volume of glass containing one gram atom of oxygen (Huggins' V_o, Stevel's V). But this progressive loosening of the network does not occur when lithium is added. As can be seen in the accompanying diagram, V_o actually *decreases* with increasing lithium additions, indicating a definite contraction of oxygen ions. For that matter, both eucryptite and spodumene form glasses with higher densities than the equivalent crystalline form.



Effect of Li_2O and Na_2O on V_o of Alkali-Silicate Glasses

By tightly binding alkali ions in the network holes, lithia additions can confer several benefits on glass, ceramic body, and enamel compositions. Among them:

- improved chemical durability
- increased hardness and abrasion resistance
- lower electrical conductivity
- lower thermal expansion



Thermal Expansion of Alkali-Borate Glasses

All of these general properties are not apparent in *all* lithia compositions.

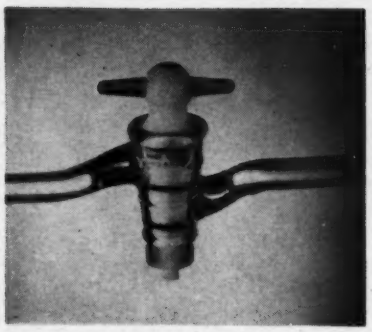
But before the practical extent of such improvements can be forecast with accuracy for a given composition, more information will be needed. As a supplier of lithium chemicals and glass grade lithium minerals to the glass industry, we are doing everything we can to develop it through a continuing exploration of lithium glass forming systems.

The fruits of this research program and our years of practical experience can be brought to bear on your problems. We'll gladly arrange discussions with our engineers. Write Foote Mineral Company, 477 Eighteen West Chelten Building, Philadelphia 44, Pennsylvania.

FOOTE MINERAL COMPANY

INDUSTRIAL LITHIUM CHEMICALS • GLASS GRADE LITHIUM MINERALS (PETALITE, SPODUMENE, LEPIDOLITE, AMBLYGONITE) • FELDSPAR IRON PYRITES • CHROMITE

NEW EQUIPMENT AND SUPPLIES



Hi-Vacuum Plug

Borosilicate glass barrel stopcock with Teflon plug has "O" rings incorporated at each end for positive seal, and is larger than conventional size to minimize possibility of leakage. Available with single oblique bore or double oblique bore.

Scientific Glass Apparatus Co., Inc., Bloomfield, N.J.

Level Indicators

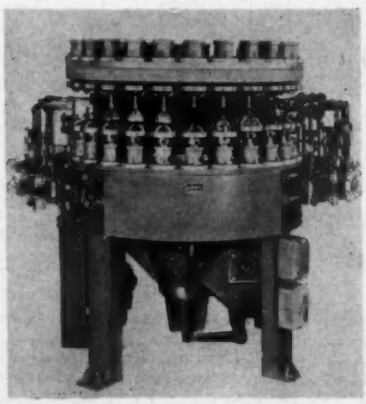
Flexible shaft level indicators said to provide deep-down control for an accurate and reliable bin level control, by preventing bulk materials from building up along the side of the bins.

Convair, Pittsburgh 26, Pa.

Stemware Splicer

Automatic glass splicer, with 24 duplex heads, that unites goblet bowl and stem foot. Available with automatic loading of parts and automatic unloading of finished goblets. Machine height: 5'8"; diameter: 5'6".

Kahle Engineering Co., 3322 Hudson Ave., Union City, N.J.



Glass-to-Weatherstrip Adhesive

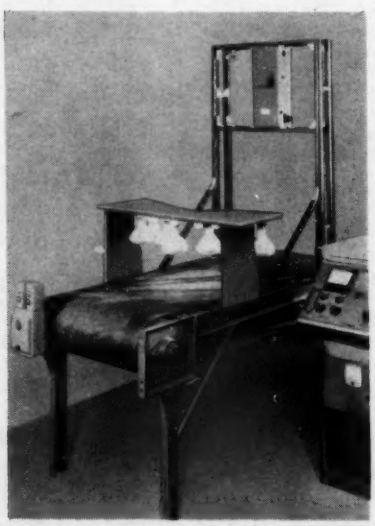
Adhesive said to provide a permanent seal for heavy, complex glazing of modern automobiles, capable of lasting the lifetime of the car. Applied to the glass and the rubber weatherstrip on windshield and backlight, it creates a permanent bond similar to vulcanizing in rubber. Claimed to withstand any atmospheric conditions in the world.

Pittsburgh Plate Glass Co., 632 Fort Duquesne Blvd., Pittsburgh 22, Pa.

Electronic Inspection

For use in production lines of the glass, food processing, textile, and plastic industries. Said to detect imperfections as small as three per cent by noting differences in light intensity between flaws and surrounding areas. Usable with conveyor belts up to 10 ft. wide; speeds up to 600 ft. per minute.

System consists of an optical scanner, with an illumination source over the conveyor that gathers information on light intensity differences; a data processor which analyzes the information; a control panel and a power supply. Actuating device for removing or marking the flaw is specially designed for each application.



Atronic Products Inc., One Bala Ave., Bala-Cynwyd, Pa.

CATALOGS RECEIVED

Centrifugal pump manual. (227 pages) Gives the general forms and types of centrifugal pumping equipment. Covers the principles of centrifugal pump operation; viscosity effects; cavitation and suction lift; temperature rise in pumps, packing and seals; installation and trouble-shooting. Illustrations. Charts and tables.

BUFFALO FORGE CO., Dept. 23, 490 Broadway, Buffalo, N. Y.

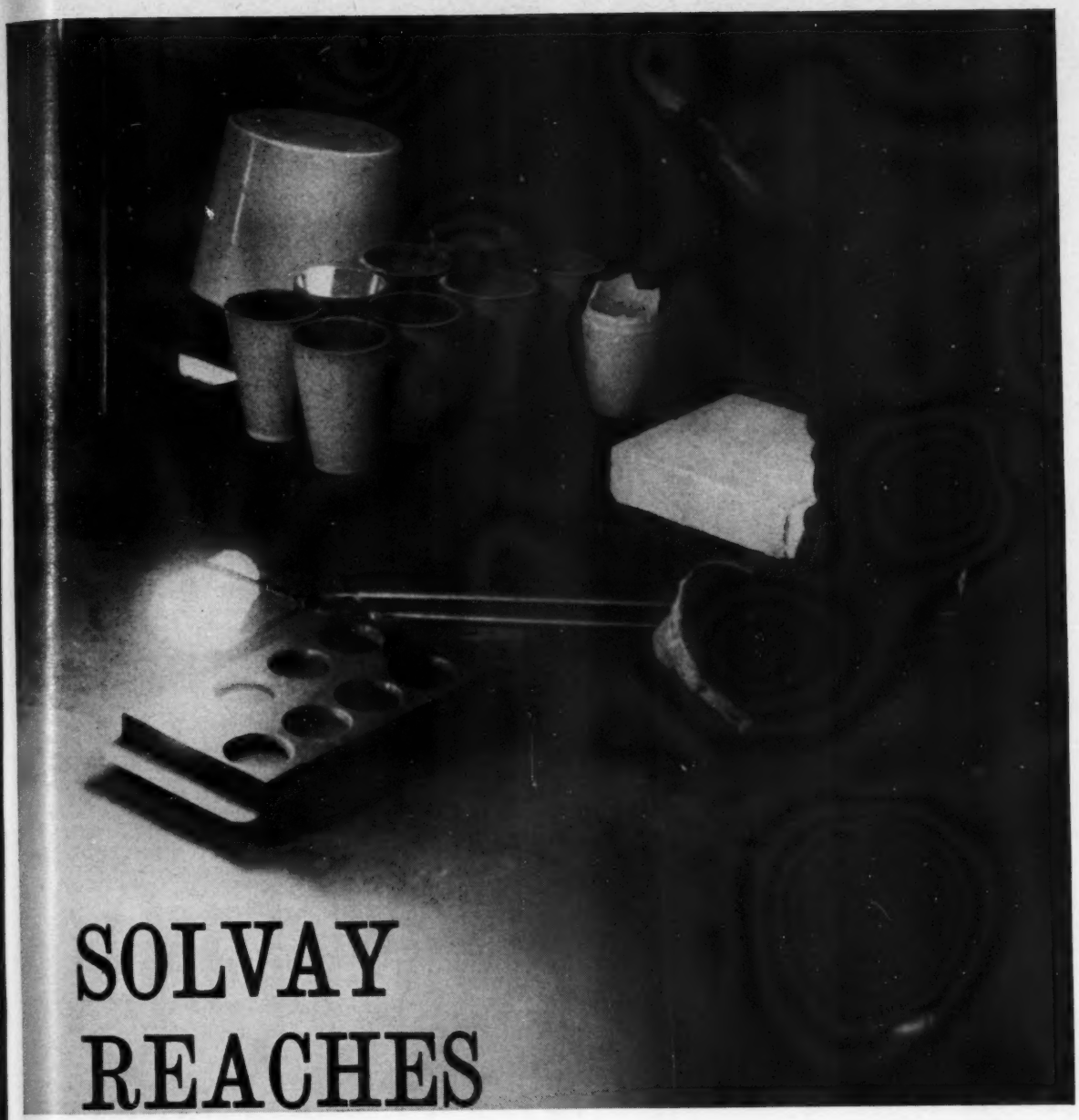
Arsenic trisulfide glass. (8 pages) Brochure states that arsenic trisulfide glass is considered better than crystalline infrared transmitting materials in various chemical, physical, thermal, and optical properties. Publication points out that this glass can be made into special lenses, correction plates, prisms, domes, wedges, or windows. Detailed drawings and specifications are included on standard cell windows for use with Beckman, Baird Associates, and Perkin-Elmer IR cells.

SERVO CORP. OF AMERICA, 111 New South Rd., Hicksville, L.I., N.Y.

Fiber glass. (52 pages) Illustrated. Designed to show the wide range of industrial applications in which fiber glass materials produced by the continuous filament and staple fiber processes can be utilized.

Contains sections on continuous filament yarn, treated yarn, staple fiber textile materials, cordage and sewing thread, scrim, mat, roving, chopped strands, milled fibers, fabrics and tapes, and standard packages for fiber glass textile fiber materials.

OWENS - CORNING FIBERGLAS CORP., Gen'l. Offices, Toledo 1, O.



SOLVAY REACHES OUT to help a customer reduce his costs

This Solvay glass technician is helping solve a complex production problem for a glass manufacturer. Here he pours a sample of glass to be tested for light transmission. With the help of Solvay glass specialists, this manufacturer quickly started economical production of his new product.

Solvay continually works to help customers raise product quality without increasing costs, or cut costs without sacrificing quality. Solvay men draw on a wealth of knowledge and practical experience gained in over 75 years of working with the glass industry plus the facilities of an outstanding glass research laboratory. These men and facilities can serve you. Why not specify Solvay on your next chemicals order?

SOLVAY® GLASSMAKING CHEMICALS

Soda Ash • Potassium Carbonate
Ammonium Bicarbonate • Mutual® Bichromates

Allied Chemical

SOLVAY PROCESS DIVISION
61 Broadway, New York 6, N.Y.

FIBER GLASS IN SUBWAY CARS

(*Continued from page 447*)

cut to pattern (Fig. 3), are placed in the mold and impregnated with a flame retardant polyester resin[3] (Fig. 4).

Care must be taken to make sure that each fiber glass mat is completely impregnated and void free before the next mat is added. The liquid resin is catalyzed[4] beforehand so that it will polymerize after the lay up is completed. The thickness of the finished product is determined by the physical properties that are required for that particular unit; this thickness is controlled by the number of plies of fiber glass mat used in the molding process. In some areas, such as the front faces, for example, Modular Molding inserts extra plies to increase the rigidity—without adding excessive weight in other areas where it is not needed.

After polymerization, the fiber glass shell is removed from the mold and then goes to a drill and routing jig (Fig. 5) where the operator routs out the window cut-outs and drills and counter-sinks the necessary mounting holes.

Stainless steel inserts are molded into the fiber glass shell and fiber glass strips are bonded to the shell with epoxy resin for additional rigidity (Fig. 6).

To make sure that all of the molded inserts are properly located, and the critical inside dimensions are maintained, the finished car front is then checked on an installation and inspection fixture which simulates the mounting structure of the car (Figs. 7, 8).

As a separate, but similar, operation, the signal light housings are molded, drilled and routed (Figs. 9, 10), and the unit is complete and ready for shipping (Fig. 11), and installation (Fig. 12).

Major advantages in using fiber glass

1. Low cost tooling.
2. Fast delivery. It is a matter of weeks from the beginning of tooling to actual delivery of first units.
3. Shatter-proof, dent-, fire-, and corrosion-proof, and highest strength-to-weight ratio of all structural materials.
4. Permanent molded-in color. Stainless-steel gray color is molded into the finished part, eliminating any painting and maintenance.

REFERENCES:

1. Gel Cote, produced by the Glidden Company, Reading, Pennsylvania.
2. Fiber glass mat, Treatment T216E, 1½ ozs/ft² produced by Owens Corning Fiberglas, Philadelphia, Pennsylvania.
3. Flame retardent resin Hetron 353, produced by Durez Plastics Division, Hooker Chemical Corporation, North Tonawanda, New York.
4. Catalyst, Methyl Ethyl Ketone Peroxide, produced by Lucidol Division, Buffalo, New York.

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CONDITIONS OF GLASS FORMATION

(*Continued from page* 433)

the conditions of glass formation he made a distinction between the large-scale stability of the random structure of the glass and the local stability of its structural units. The latter units, he wrote, "demand mixed chemical binding forces which are partly covalent and partly of ionic nature." Smekal assumed that the bonding type of a substance in a glassy state may differ fundamentally from that of the substance in its crystalline state.

This use of the "bond type" provides a convenient parameter for explaining phenomena for which no other explanation could be given. Thus Smekal explained glass formation on the basis that the liquid on cooling and supercooling assumes a bond type which is suitable for the glassy but not for the crystalline state.

Smekal[27] first published in 1942 his concept that glass formation is the result of "mixed bonds" and it must have had a certain appeal because only one year later A. Dietzel[28] (1943) used it for explaining the anomaly that within a certain temperature region silica glass expands on cooling and becomes stronger on heating. He assumed that heating causes the mixed bond to change into a more ionic bond which provides greater mechanical strength.

When V. M. Goldschmidt[29] provided a new tool, namely, the crystal chemical approach to the formation and the structure of glasses, it was applied almost exclusively to silica and silicates but not to his fluoride glasses. Singling out silica as the prototype of glass formers led to some confusion with respect to the real meaning of the chemical bond in glasses and crystals. Vitreous silica, the first glass whose structure was determined by X-ray methods, consists of two elements for which the "valency" and the "coordination number" happen to be identical. Silicon in the classical sense is tetravalent and in the modern crystal chemical sense it has the coordination number of four. Oxygen is "divalent" and in silica it had the coordination number of two. If structural studies in the field of glass formation would have been centered around beryllium fluoride there would have been no danger of confusing atomic and ionic descriptions. Scientists would probably not have spoken of double bonded and single bonded fluorine because fluorine has the valency of one. Because of this coincidence we do not find a clear cut distinction between the two ways of describing matter but find the same author using both descriptions interchangeably. We find the term electronegativity, a property of a neutral atom, applied to elements which are treated as ions in the structure. In the same way we find the dissociation energies of compounds into neutral atoms applied to conditions where the same author uses the ionic description. For example, lead oxide in a glass is a "divalent" atom from a classical point of view.

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- ☐ 3. Glass-to-molybdenum seals
- ☐ 4. Battery jars

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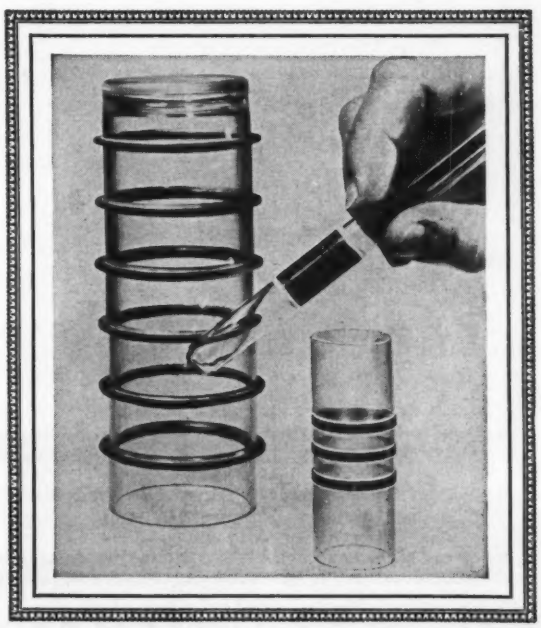

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However, from a crystal chemical viewpoint, it participates in the structure as an ion which has the charge 2+ but a coordination number which is higher than two, namely, eight in the PbO crystal.

The role which the nature of the chemical bond is supposed to play in glass formation is rather obscure. Considering the great variety of substances which form glasses it is difficult to understand how scientists could ever consider the bond type as a factor which could determine the stability of a substance in the vitreous state. **(Part I to be continued in Sept.)**

62nd A.C.S. MEETING

(*Continued from page* 439)

A Method for the Measurement of Thermal Diffusivity to 1000°C.

By William A. Plummer, Donald E. Campbell, and A. A. Comstock (deceased),
CORNING GLASS WORKS, CORNING, NEW YORK.
Presented by Mr. Plummer.

A non-steady state was developed and used to measure the thermal diffusivity of glass in the solid state, thus allowing measurements somewhat beyond the annealing point. The equipment needed was not elaborate and the sample preparation relatively simple. The equipment consisted of flat heating elements (in this case five-mil chromel sheet), rods for feeding power to the heating elements, a step-down transformer, a means for clamping the sandwich, a simple furnace for containing the sample, and an inexpensive temperature controller. The sample consisted of a 3" x 5" sandwich constructed in the following manner: one-inch thick sample, chromel heat sink, 0.25 inch sample, chromel heat source, 1.25-inch sample. This type of construction resulted in a sandwich as symmetrical as possible about the heater.

The diffusivity was determined by starting the heating at zero time and measuring and recording the temperature rise of both the heat source and the heat sink. The mathematical solution was such that the ratio of these temperatures is a function only of the modulus,

$$x/2\sqrt{a\,t}.$$

where x is the distance separating the source and sink, a the diffusivity, and t the time. The assumptions on which the equations were based and the experimental limitations of the method were discussed.

Wednesday Afternoon

Chairman Guy E. Rindone, Pennsylvania State University, University Park, Pennsylvania.

Variation of Refractive Indices and Densities in Tempered Glass.

By Robert Gardon and S. F. Whiteside,
GLASS RESEARCH CENTER, PITTSBURGH PLATE GLASS COMPANY, PITTSBURGH, PENNSYLVANIA.
Presented by Mr. Gardon.

A knowledge of density distributions in tempered glass

is of interest in studying the tempering process. The density-heterogeneity of tempered glass has previously been demonstrated by Plumat, who fractionated crushed samples of annealed and tempered glass by centrifugation and showed that tempered glass was not only lighter, but also more heterogeneous than annealed glass.

The object of this paper was to determine not only the spread of densities, but also the location of each density-fraction within the tempered plate. Because the density and refractive index of a glass are uniquely related, this was accomplished by a Schlieren technique, which measured index-gradients and hence also density-gradients, from which densities were obtained by integration. For the one-dimensional index variation of interest, a Philpot-Swensson type Schlieren system was particularly convenient and suitable. Since its sensitivity is adjustable over a wide range, it was equally useful for measuring density distributions in tempered specimens of glass and in small fragments. It thus afforded a method for studying the changes in local densities that accompany the release of temper stresses.

It was shown that surface layers of a tempered plate, which are usually cooled through the transformation range more rapidly, solidify into a more expanded structure than interior layers of glass. However, the lower stress-free density of the surface layers is more than offset by the elastic compaction due to the compressive temper stresses in those layers. Thus, the density and refractive index of unbroken tempered glass are always highest near the surface. This fact can be put to use for measuring temper stresses, as was later discussed in a subsequent paper by Mr. Acloque.

Stress Measurements by "Mirage-Transmission" or "Mirage-Reflection" in Tempered or Bent Glass.
By P. Acloque,

CIE DE SAINT GOBAIN, PARIS, FRANCE.

The stress system which exists in plates or sheets of tempered glass, as well as the one which results from flexure, cannot be measured by ordinary polariscopic methods, using the whole piece, because of two difficulties:

1. With observation perpendicular to the surface, the path of light lies along the optic axis because the stress is isotropic in each plane parallel to the surface.
2. With observation oblique to the surface, the integral of birefrigence is zero owing to mechanical equilibrium of the stress system.

This paper developed two new polariscopic analyses that overcame these difficulties. The first, called "mirage-transmission," took advantage of the fact that along a general direction very inclined to the stress planes the path of light is curved, thereby making the integral of birefrigence different from zero. The second used the refraction-limit wave originating from a medium of greater index in contact with the glass surface. This wave returned to the medium after a very short path in the adjoining layer of glass with its intensity greatly enhanced by the effect of "mirage-reflection." A short description of the apparatus for these methods was presented.

The Microstructure of Soda-Lime Glass Surfaces.
By R. M. Tichane and *G. B. Carrier,*

CORNING GLASS WORKS, RESEARCH AND DEVELOPMENT DIVISION, CORNING, NEW YORK.
Presented by Mr. Tichane

Electron micrographs were made of soda-lime glass surfaces after several chemical treatments and a flame-polishing treatment. Compared to a control sample of fractured glass, the flattest surfaces were formed by hydrofluoric and phosphoric acids, sodium citrate, the disodium salt of ethylenediaminetetraacetic acid, and a flame polish-water wash combination. Caustic solutions tended to roughen the glass surface and leave residues. Selected electron micrographs were shown to illustrate the effect of these treatments on soda-lime type glass.

The Variation of Strength of Acid Polished Glass with Surface Area of the Specimens Tested.
By Charles H. Greene,

STATE UNIVERSITY OF NEW YORK COLLEGE OF CERAMICS, ALFRED UNIVERSITY, ALFRED, NEW YORK

Experiments on samples of soda lime glass ranging in size from fibers to 3″ x 12″ strips indicated that there was less variation in the average strength with changes in the size of the sample tested than would be predicted from the random variations observed in testing sets of identical samples. The conditions giving maximum strength with drawn window glass were investigated and consideration given to errors in the sample beam formula resulting from large deflections. Instantaneous photographs taken immediately after failure showed that breaks originated both at the edges of flat laths and on the lower surface. Simultaneous failure at two points was observed occasionally in samples having weak (badly flawed) edges.

Fracture Velocity of Glass in the Fatigue Range.
By Errol B. Shand,

TECHNICAL CONSULTANT, CORNING, NEW YORK.

A critical review of present theories of the fracture of glass revealed differences in basic concepts which are not readily reconciled. These differences suggested a deficiency of ascertained facts and perhaps a lack of correlation of available facts as well. In particular the matter of stress fatigue has never been adequately explained. Consequently, it is pertinent to investigate neglected areas of research in this field. The subject of this study was, therefore, the fracture velocity in the fatigue range. Although these velocities are associated with the initial phases of fracture, they have been somewhat neglected in favor of the more spectacular velocities which occur in the final phase of the process. The results obtained in this paper did not answer the question of stress fatigue,

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but they did throw additional light on the mechanism of brittle fracture.

When glass is broken under a low stress, the initial rate of crack propagation may be extremely slow. This rate increases with the growth of the crack until a condition of instability is reached, after which the velocity passes rapidly to a terminal value of the order of 1500 meters per second.

This paper presented an interesting approach to the problem of stress fatigue. A method was developed for the determination of fracture velocities as a function of relative crack-tip stress from the stress-time curve of fracture (velocities of glass broken in air and in vacuum converge at a velocity of the order of 10 mm. per second, with this convergence being considered the upper limit of the fatigue process). Relationships between local stress, crack geometry, and fracture velocity were presented in generalized form.

Strain energy release rates were computed as a function of crack velocity. For glass broken in air under low stress this energy corresponded with the surface energy, but in vacuum or in air under high stress this energy was 10 to 15 times greater. The hypothesis advanced to explain this condition is that two criteria of brittle failure are implied by the Griffith theory, one based on energy balance, the other on the stress required to break ionic bonds. The former criterion governs fracture at low velocities in air and the latter at the upper limit of the fatigue range and in vacuum.

It was concluded that within the limited scope of this study a method was developed for determining the fracture velocities of glass in the fatigue range. This method is applicable to other ceramic bodies. Generalized relationships for fracture times and fracture velocities were derived analytically. Strain energy release curves as a function of fracture velocity were computed. Evidence has been found of the existence of two criteria of brittle fracture in the tensile failure of glasses. A re-examination of the Griffith theory confirmed this conclusion.

ROSS COFFIN PURDY AWARD

The Ross Coffin Purdy Award was presented to S. D. Stookey, Corning Glass Works, a prominent member of

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the Glass Division, for his explanation of nucleation in the book "Ceramic Fabrication Processes," edited by W. D. Kingery and published jointly by the Technology Press of the Massachusetts Institute of Technology and John Wiley and Sons, Inc., New York; and Champan and Hall, Ltd., London. It was quite appropriate that the plaque symbolizing the Purdy Award was photosensitive glass because Dr. Stookey's work has been very important in the field of photosensitive glass, and his development of Pyroceram was in part an outgrowth of that work. The Glass Division heartily congratulated Dr. Stookey on this well-earned award.

GLASS DIVISION FALL MEETING, 1960

The Fall Glass Meeting of the Glass Division will be held at Bedford Springs Hotel, Bedford, Pennsylvania, October 12-14, 1960. The program will feature a Workshop on "Methods for Studying Crystallization Processes and Phenomena," with Howard Swift, Libbey-Owens-Ford Glass Company, Toledo, Ohio, as chairman. The ladies' committee will be under the chairmanship of Mrs. Charles Gum. Mr. Charles Gum, Ohio Lime Company, Pittsburgh, Pennsylvania, will be chairman of the Golf Committee.

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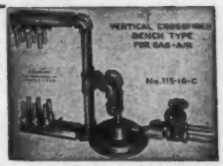

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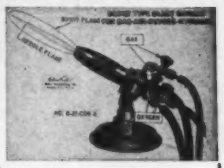

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